

# Structural Variety of Iron Carbonyl Clusters Featuring Ferrocenylphosphines

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Dedicated to Prof. Dr. Christoph Janiak on the occasion of his 60th birthday.

The reaction chemistry of Fe<sub>2</sub>(CO)<sub>9</sub> (**10**) with ferrocenenyl dichlorophosphines of different substitution is discussed. Single FcPCl<sub>2</sub>, (**5**) as well as 1,1'- (**6**) and 1,2- (**9**) difunctionalized phosphines were used, of which **6** and **9**, were prepared in a novel straightforward synthetic process. Substrate **5** gave butterfly-shaped Fe<sub>2</sub>(CO)<sub>6</sub>( $\mu_2$ -Cl)( $\mu_2$ -PFcCl) and Fe<sub>2</sub>(CO)<sub>6</sub>( $\mu_2$ -PFcR<sup>1</sup>)( $\mu_2$ -PFcR<sup>2</sup>) (R<sup>1</sup>, R<sup>2</sup> = Cl, H). In addition, *nido*-Fe<sub>3</sub>(CO)<sub>10</sub>( $\mu_3$ -PFc) and *nido*-Fe<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ -PFc)<sub>2</sub> were obtained. 1,1'-Functionalized **6** bridges both ends of the Fe<sub>2</sub>(CO)<sub>6</sub> entity. Therein, the so far smallest non-binding P···P distance (2.7674(12) Å) between both 1,1'-substituents is observed. Additionally, an *'organometallic octabisvalene'*, containing two [2]ferrocenophane entities was obtained. The eight-membered cyclic structure is

# Introduction

Phosphorus-bonded iron carbonyl clusters have intensively been studied, due to, for example, their rich structural variety,<sup>[1,2]</sup> specific tuning of their electronic properties<sup>[3,4]</sup> and their facile cluster periphery functionalization.<sup>[5–7]</sup> Their use as, *e.g.* hydrogenase biomimetics,<sup>[5,6b,8]</sup> reduction catalysts<sup>[9]</sup> and antibacterial agents have been explored.<sup>[10]</sup> It was in this respect, that 1,1'-bisphosphino ferrocenes  $Fe(\eta^5-C_5H_4PR_2)_2$  (R=alkyl, aryl), com-

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twisted by  $35.31(9)^{\circ}$  regarding their ferrocenyl axis. Usage of  $1,2-(PCI_2)_2$  functionalized **9** produced two isomers of a P–P connected dimer, which coordinates towards two independent Fe<sub>2</sub>(CO)<sub>6</sub> fragments in a novel  $\mu,\mu',\kappa^8$  or bis( $\mu,\kappa^4$ ) fashion, resulting in a *meso* isomer with a planar core, and a *racem* mixture, possessing a pocket-type structure. The latter shows the so far shortest observed P···P distance of 2.950(7) Å between two *ortho* P atoms of a ferrocenyl backbone. The results confirm that the geometric properties of ferrocenyls featuring 1,1'- and 1,2-substitution patterns are not comparable with phenyl-based analogues. X-ray single crystal solid state structures, and DFT calculations were carried out.

monly used as chelating ligands for mono and multimetallic metal carbonyl building blocks,<sup>[5,6,7,11]</sup> can interact with their iron center towards the coordinated metal M in a  $\kappa^3$  mode. Especially, for M = Fe, Ni an inverse charge transfer from Fe<sup>II</sup> to M<sup>I</sup> occurs.<sup>[4]</sup> Ferrocenyl groups are commonly used as redoxactive probes to investigate the conducting properties of organic or organometallic conjugated linkers and their ability to allow electronic communication in mixed-valent redox states of such molecules.<sup>[12]</sup>

However, the so far chosen aryl and alkyl functionalities of the  $Fe(\eta^5-C_5H_4PR_2)_2$  starting materials limit the coordination mode for each P donor towards the metal carbonyl fragments to a  $\kappa^1$  mode (Table S1). Hence, a direct incorporation of the phosphorus atom into the cluster core cannot be accessed. The phenyl analogues instead, are known for their variety of phosphinidene (=phosphanylidene) and phosphido clusters,<sup>[1]</sup> where the required PhPCl<sub>2</sub> educts are readily available. Attaching ferrocenyl groups to phosphinidene or phosphide motifs directly would require FcPCl<sub>2</sub> as a starting material, which was hitherto difficult to synthesize. Hence, the so far only reported example of a cluster resulting from a reaction with FcPCl<sub>2</sub>, contained PFc and PFc<sub>2</sub> functionalities, due to the difficulties within the purification process of the dichlorophosphine.<sup>[13]</sup> Thus, alternative strategies to link Fc substituents to Pcontaining metal carbonyl fragments involved additional spacer groups, as found in e.g.  $Fe_2(CO)_6(\mu_2-P(CH_2Fc)H)_2$ .<sup>[14]</sup>

Recently a synthetic methodology was reported to obtain  $FcPCI_2$  in analytical pure form from  $FcPH_2$ .<sup>[15]</sup> allowing us to investigate its reaction chemistry towards  $Fe_2(CO)_9$  and  $Co_2(CO)_{8r}$  respectively. Within these reactions *nido* phosphini-

dene clusters Fe<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ -PFc)<sub>2</sub> and Co<sub>4</sub>(CO)<sub>10</sub>( $\mu_4$ -PFc)<sub>2</sub> were synthesized.<sup>[16]</sup> For the sole preparation of edge-opened cluster Fe<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ -PFc)<sub>2</sub> a comparably long reaction time of 2 h at 50 °C was required. It was, however, shown for phenyl-based substrates that formation of such bipyramidal phosphinidene clusters is a stepwise process, involving several intermediates with different core geometries.<sup>[1]</sup> These species will be accessed herein for ferrocenyl derivatives.

The new protocol for the synthesis of FcPCl<sub>2</sub> also enables a novel access to bis-PCl<sub>2</sub>-functionalized ferrocenes, based on 1,1'-<sup>[17]</sup> and 1,2-substitution pattern,<sup>[18]</sup> which are so far synthesized via the P(NEt<sub>2</sub>)<sub>2</sub>/HCl route. The latter has only been mentioned once in literature.<sup>[18]</sup> The ferrocenyl core in both type of compounds provides unique geometric properties that cannot be achieved by condensed aromatics (Figure 1, Figure S1, Figure S2).<sup>[19,20]</sup> Additionally, the conformational flexibility around the Cp-Fe bond of the 1,1'-substituted sandwich allows for the synthesis of di-<sup>[5,7,21,22]</sup> and polymeric complexes<sup>[23]</sup> and the bending of the backbone for unique connectivity modes.<sup>[24]</sup> The 1,2-substitution pattern (Figure 1) exhibits an increased P-P distance and a wider opening angle compared to 1,2 phenylenes, whereby a ferrocenyl annelation still occurs. Such planar-chiral motifs are also known to introduce chirality.<sup>[25]</sup>

Due to the limited accessibility of FcPCl<sub>2</sub> its use as PFc source within metal carbonyl cluster synthesis remained unexplored, except to our recent investigations on iron and cobalt *nido* phosphinidene clusters Fe<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ -PFc)<sub>2</sub> and Co<sub>4</sub>(CO)<sub>10</sub>( $\mu_4$ -PFc)<sub>2</sub>.<sup>[16]</sup> Hence, fundamental research needs to be carried out to investigate the impact of the unique geometric and electronic properties of the ferrocenyl unit within that field.

Herein, we discuss the reaction chemistry of Fe<sub>2</sub>(CO)<sub>9</sub> with Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>PCl<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) (5), Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>PCl<sub>2</sub>)<sub>2</sub> (6) and Fe( $\eta^5$ -C<sub>5</sub>H<sub>3</sub>-1,2-(PCl<sub>2</sub>)<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) (9). The chemical and physical properties of the clusters synthesized were investigated by spectroscopic, electrochemical, computational methods, as well as by single-crystal X-ray diffraction analysis.

# **Results and Discussion**

### Chlorophosphine Synthesis

Iron carbonyl phosphide and phosphinidene clusters are accessible by reacting, for example, chlorophosphines  $(\text{RPCl}_2)^{[1]}$  or phosphines  $(\text{RPH}_2)^{[14,28]}$  with an excess of Fe<sub>2</sub>(CO)<sub>9</sub>, of which the latter procedure requires higher reaction temperatures and longer reaction times, *e.g.* 90 °C for 3 days, to enable the formation of H<sub>2</sub>.<sup>[14]</sup> The reaction with chlorophosphines proceeds more rapidly at ambient temperature, whereby an excess of Fe<sup>0</sup> acts as the oxidant accompanied by the precipitation of FeCl<sub>2</sub>. Furthermore, structurally more divers products are accessible, due to a kinetic product formation at lower reaction temperatures.<sup>[1]</sup>

Hence, dichloroferrocenylphosphines **5**, **6** and **9** were synthesized from phosphonates **1**, **2** and **7**, which were reduced to phosphines **3**, **4** and **8** and quantitatively converted into dichlorophosphines upon treatment with a toluene phosgene solution (Scheme 1, Experimental Part).<sup>[15]</sup>

Phosphonates 1 and 2 are accessible from ferrocene (FcH; Fc = Fe( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>)( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)) upon mono- and dilithiation, respectively; the 1,2-substitution pattern was established upon *ortho*-lithiation of 1. Compound 7 is the second of its type, following its *i*Pr analogue.<sup>[29]</sup> Noteworthy, the so far only reported example of 8 was based on reduction of Fe( $\eta^{5}$ -C<sub>5</sub>H<sub>3</sub>-1,2-(PCl<sub>2</sub>)<sub>2</sub>)( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>) (9), which in turn was obtained upon reaction of P<sup>III</sup> amidates with HCl.<sup>[18]</sup> However, the herein described procedure does not require the synthesis of further chloro phosphoramidates, which are highly sensitive towards acidic conditions, and instead can be applied on commercially available chloro phosphates.

#### **Cluster Synthesis**



**Figure 1.** Unique geometrical properties of the ferrocenyl- compared to phenyl-based motifs represented by their *ypso* (top) and P--P distance (bottom) in their non-bended/distorted shapes. (Values were calculated<sup>[26]</sup> based on reference<sup>[27]</sup> and herein reported compounds).

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 $\begin{array}{c} \overbrace{Fe}^{O} \\ Fe \\ Fe \\ R \\ 1 (R = H) \\ 2 (R = P(O)(OEt)_2) \\ (R = H) \\ 1 (R = H) \\ 2 (R = P(O)(OEt)_2) \\ (R = P(O)(OEt)_2) \\ (R = P(O)(OEt)_2) \\ (R = P(O)(OEt)_2) \\ (R = H) \\ (R =$ 

**Scheme 1.** Synthesis of dichloroferrocenylphosphines **5**, **6** and **9**. *i*) Li[AlH<sub>4</sub>], ClSiMe<sub>3</sub>, THF, 45 °C, 18 h; *ii*) COCl<sub>2</sub> (1.9 *M* in toluene), CH<sub>2</sub>Cl<sub>2</sub>, 25 °C; *iii*) THF, BuLi, TMEDA, ClP(O)(OEt),.<sup>[15]</sup>

The dichlorophosphines **5**, **6** and **9** were reacted with an excess of  $Fe_2(CO)_9$  (**10**) in different ratios in toluene (see below and the Experimental Section). The mixtures were placed in a 45–50 °C pre-heated oil bath to control reaction time precisely. Afterwards, reaction mixtures were rapidly cooled to ambient



temperature and subsequently filtered through a pad of Celite. Purification was achieved by column chromatography with silica, with the crude material pre-coated on silica. All obtained clusters were eluted with hexane/toluene mixtures after  $Fe_3(CO)_{12}$ .

Our recent findings showed that the reaction of **5** with a 7fold excess of **10** gave the trimetallic phosphinidene cluster *nido*-Fe<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ -PFc)<sub>2</sub> (**14**) as the sole product (42% yield), as the thermodynamically most favored product within a 2 hour reaction time.<sup>[16]</sup> It is, however, known that cluster formation is a multi-step process, including several mono- and bimetallic intermediates.<sup>[1a]</sup> We were interested on how the ferrocenyl group, with its sterically and electronically modified backbone,



Scheme 2. Reaction of 5 with  $Fe_2(CO)_9$  (10) giving compounds 11–14. (*i*) Toluene, 0.5 h, 45 °C, ratio of 5:10=1:6; a) the main isomer is shown; b)  $t=2 h_r^{(16)} c$ ) ratio 5:10=1:1; a relative configuration is shown, for absolute configurations see Figure 2).

influences the geometry and chirality of these intermediates and reduced the reaction times to 0.5 hours (Scheme 2). Therein, Fe<sub>2</sub>(CO)<sub>6</sub>( $\mu_2$ -CI)( $\mu_2$ -PFcCI) (11), Fe<sub>2</sub>(CO)<sub>6</sub>( $\mu_2$ -PFcR<sup>1</sup>)( $\mu_2$ -PFcR<sup>2</sup>) (12a, R<sup>1</sup>=R<sup>2</sup>=CI; 12b, R<sup>1</sup>=CI, R<sup>2</sup>=H; 12c, R<sup>1</sup>=R<sup>2</sup>=H), *nido*-Fe<sub>3</sub>(CO)<sub>10</sub>( $\mu_3$ -PFc) (13), and *nido*-Fe<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ -PFc)<sub>2</sub> (14) were isolated.

It is known that by the reaction of Fe<sub>2</sub>(CO)<sub>9</sub> with RPCI<sub>2</sub> (R = *e.g.* Ph) at first mono-nuclear RCI<sub>2</sub>P $\rightarrow$ Fe(CO)<sub>4</sub> is formed, which on subsequent treatment with Fe<sub>2</sub>(CO)<sub>9</sub> produces Fe<sub>2</sub>(CO)<sub>6</sub>( $\mu_2$ -Cl)( $\mu_2$ -PPhCl), isostructural to 11.<sup>[1]</sup> It should be noted that P $\rightarrow$ C bond cleavage can occur, if halide substituents are absent.<sup>[30]</sup> During the course of the reaction, replacement of the  $\mu_2$ -Cl entity by FcPClx results in 12. That replacement of the bridging chloride is preferred over P $\rightarrow$ Cl was shown recently.<sup>[1a,31]</sup> Reaction of 11 with Fe<sub>2</sub>(CO)<sub>9</sub> probably also forms homotrinuclear *nido*-Fe<sub>3</sub>(CO)<sub>10</sub>( $\mu_3$ -PFc) (13) (Scheme 2). As shown, cluster 14 is the thermodynamically preferred product within this reaction and most probably formed from all precursors.

Butterfly-type cluster **12** was obtained as a mixture of 3 species, in which the *exo*-Cl atoms have subsequently been replaced by H atoms. Such an exchange has sparsely been observed, but can be explained by a P-anion formation in the presence of an excess of  $Fe^{0,[32]}$  Such a negatively charged phosphide may act as an intermediate species, prior to its subsequent coordination towards  $Fe_2(CO)_x$ .

The relative configuration of the PFcX entity towards the butterfly core in dinuclear  $Fe_2(CO)_6(\mu_2-CI)(\mu_2-PFcCI)$  (11) and  $Fe_2(CO)_6(\mu_2-PFcR)_2$  (12 a–c) resulted in mixtures of diastereomers (Scheme 2, Figure 2). For 11, the ratio of *axial*- and *equatorial*-Fc groups (*a/e* ratio) is approximated to ~3.3:1 by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. According to the so far observed trend,<sup>[37]</sup> an



**Figure 2.** <sup>31</sup>P (top) and <sup>31</sup>P{<sup>1</sup>H}</sup> NMR spectra (bottom) of mixtures of derivatives and isomers of **12**. The dashed backbone represents the  $Fe_2(CO)_6$  unit as observed within the crystal structure of *a*,*a*-**12 a** (**A**) shown in Figure 3. (To avoid confusion caused by the different priority of H and Cl compared to a ferrocenyl group, the expressions *a* (axial) and *e* (equatorial) refer to the Fc group; Cl-bonded P atoms are prioritized over H-bonded ones.).



equatorial P–Cl bond, *i.e.* and *axial* alkyl/aryl group, results in a high-field shifted set of signals for <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P nuclei. It is furthermore known that the kinetically favored isomer bears the aryl/alkyl groups in *axial* position, *i.e. endo* regarding the butterfly core. That the *a*-isomer is the generally preferred configuration was also shown for other PCIR groups (R=alkyl, aryl) in  $\mu_2$ -Cl and  $\mu_2$ -SR iron carbonyl butterfly structures.<sup>[28]</sup> Compound 11 follows both trends. Based on <sup>31</sup>P{<sup>1</sup>H} NMR studies the signal of the major isomer was observed at 255.5 ppm (*a*-11) and the kinetically less-favoured *e*-11 isomer at 263.9 ppm (Table 1, see below).<sup>[28]</sup> The ascribed ratio of configurations is additionally supported by the results of single crystal structure determinations of *a*-11 and *a,a*-12a (Figure 3). Analysis of the ratio of isomers and absolute configurations of

Table 1. <sup>31</sup> P{ <sup>1</sup> H} respective <sup>31</sup> P NN	NMR data (p /IR signals for bu	pm) for <b>11–20</b> utterfly-type specie	and multiplic es <b>12 a–c</b> .	ity of the
Compound	lsomer <sup>[a]</sup>	<sup>31</sup> P{ <sup>1</sup> H}	<i>Mult</i> <sup>31</sup> P{ <sup>1</sup> H}	<i>iplicity</i> <sup>31</sup> P
FcPCI <sub>2</sub>				
11	а	225.5	S	
	е	263.9	S	
12 a (Cl,Cl)	a,a	247.4	S	S
	a,e	255.0 (e)	d	d
		245.3 (a)	d	d
	e,e	254.4	S	S
12b (Cl,H)	a,a	248.5 (P <sup>CI</sup> )	d	dd
		72.3 (P <sup>H</sup> )	d	dd
	e,a	268.9 (P <sup>ci</sup> , <i>e</i> )	d	dd
		75.7 (P <sup>H</sup> , a)	d	dd
12c (H,H)	e,e	83.4	S	dd
13		452.1	S	
14		316.4	S	
1,1'-(PCl <sub>2</sub> ) <sub>2</sub> -Fc				
15 (H,H)		55.5	S	
16 (H,Cl)		227.0 (P <sup>CI</sup> )	d	
		52.9 (P <sup>H</sup> )	d	
17 (Cl,Cl)		216.0	S	
18		139.1	S	
1,2-(PCl <sub>2</sub> ) <sub>2</sub> -Fc				
19		238.2 (P <sup>CI</sup> )	dd	
		118.7 (P <sup>P</sup> )	dd	
20		277.1 (P <sup>cl</sup> )	d	
		169.9 (P <sup>P</sup> )	d	

[a] *a* and *e* refers to the position of the Fc substituent with respect to a butterfly-type  $Fe_2(CO)_6$  motif. Fc represents all types of substituted ferrocenes.



Scheme 3. Reaction of 6 with  $Fe_2(CO)_9$ , resulting in the formation of clusters 15–18. (*i*) 6 (1 eqiv), 10 (5 equiv), toluene, 45–50 °C, 1 h; a) 6:10 ratio of 1:14.

diastereomers for **12a–c** is given below. Single crystal X-ray structures of phosphinidene clusters **13** and **14** confirm their proposed structures (Figure 4).

Bis(dichlorophosphine) **6** was reacted with a 5-fold excess of Fe<sub>2</sub>(CO)<sub>9</sub> under similar conditions (toluene, 45–50 °C for 1 h; Scheme 3). To the best of our knowledge, Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>PCl<sub>2</sub>)<sub>2</sub> (**6**) has not been used in reactions with either metal clusters or metal carbonyl compounds to date. Column chromatographic work-up gave clusters **15–18**, which were all identified by NMR spectroscopy and single crystal X-ray diffraction analysis (Figure 5 and Figure 6). Compounds **15–17** exhibit a butterfly-type structure, similar to **12a–c**, whereby solely one ferrocenyl fragment chelates to the Fe<sub>2</sub>(CO)<sub>6</sub> units in a  $\mu', \kappa^4$  fashion. Cl-substituted **17** was obtained as the main product (8%, Scheme 3). Compounds **16** and **15** were obtained, in which one and two chloride atoms were replaced by hydrogen (Figure S7), respectively, similar to **12a–c**.

In addition, compound **18** was identified possessing two [2] ferrocenophane fragments that act as bridging ligands for two Fe<sub>2</sub>(CO)<sub>6</sub>P<sub>2</sub> butterfly building blocks in a  $\mu_{,}\mu'_{,}\kappa^{4}$  fashion. Especially the P–P bond within the [2]ferrocenophane moiety is an uncommon feature and is usually obtained upon reduction of a chlorophosphine with magnesium.<sup>[33a,34]</sup> Given the stability of P–Fe(CO)<sub>x</sub> bonds, it is very unlikely that **15–16** re-open their butterfly structure, reassembling giving **18**. Thus, it is more likely that an open-butterfly **12**-type structure has initially been formed, followed by the P–P bond formation with an excess of Fe<sub>2</sub>(CO)<sub>9</sub> acting as the reducing agent.

Changing the **6**:Fe<sub>2</sub>(CO)<sub>9</sub> ratio from 1:5 to 1:14 slightly increases the yield of **17**, whereby neither the formation of **15**, nor **16** was observed, and the yield of **18** remains similar. The low overall yield might also be due to the formation of poorly soluble polymers, based on  $\mu,\mu',\kappa^4$  coordination modes. In case of dppf formation of linear chains based on a  $\mu,\kappa^2$  connectivity have been reported.<sup>[23]</sup> The nature of the PCl<sub>2</sub> groups, however, allows for further coordination modes, resulting in cross-linking and hence insoluble species.

The use of planar chiral 1,2-substituted ferrocenyl phosphines as ligands for metal carbonyls is not well developed. They are so far limited to 1,2-(PPh<sub>2</sub>)<sub>2</sub> derivatives coordinating to Mo(CO)<sub>4</sub> or Mn( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)CO<sup>[35]</sup> fragments, where a more complex coordination behavior of the P donor atoms is excluded, similarly to dppf. Hence, the 1,2-(PCl<sub>2</sub>)<sub>2</sub>-substituted ferrocene Fe( $\eta^5$ -C<sub>5</sub>H<sub>3</sub>-1,2-(PCl<sub>2</sub>)<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) (9) was synthesized in order to investigate how a change of the P-··P geometry from 1,1' to 1,2 (Figure 1) influences the resulting cluster geometry.

Compound **9** was reacted with 14 equiv. of  $Fe_2(CO)_9$  (**10**) (Scheme 4). Neither for ferrocenes nor non-organometallic substrates, the reaction of a 1,2-bis(dichlorophosphines) with any homoleptic metal carbonyl has, to the best of our knowl-edge, been investigated yet.

Compared to phosphines **5** and **6**, where overall yields of 29% (**11–14**) and 13% (**15–18**) were obtained, the 1,2-ferrocenyl substitution pattern produced less than 1% of a mixture of **19** and **20** (Experimental Part). Due to an unsymmetrical substitution pattern at the phosphorus atom planar chirality is established in both compounds. Compound **19** 



Scheme 4. Reaction of 9 with  $Fe_2(CO)_9$  to give 19 and 20. (i) toluene, 45–50  $^\circ C,$  1 h.

assembles a racemic mixture of  $S_{p^-}$  and  $R_p$ -configured ferrocenyls resulting in a *meso*-isomer. Contrary, the structure of **20** features only ferrocenyls possessing an equal configuration  $(S_p, S_p)$  or  $(R_p, R_p)$ . Based on the low amount of product analysis of **19** and **20** is limited to solid state structures obtained via single crystal X-ray diffraction, represented in Figure 7 and Figure 8, respectively.

#### NMR and IR Analysis

Clusters **11–20** were identified by various NMR techniques (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>31</sup>P and <sup>31</sup>P{<sup>1</sup>H}). Analysis via IR spectroscopy and elemental analysis was limited to **11**, **13** and **14** that could be isolated in a pure form and in substantial amounts. Compounds **12a–c** and **15–17** were obtained as a mixtures of H- and Cl-functionalized phosphides that could be hardly be separated (see the Experimental Section).

The  ${}^{31}\text{P}$  and  ${}^{31}\text{P}\{{}^{1}\text{H}\}$  chemical shifts are the most indicative parameter to identify the cluster core structures and P-substitution pattern (Table 1).  ${}^{31}\text{P}\{{}^{1}\text{H}\}$  signals of all herein observed P-entities occur low-field-shifted in the order P–H (52–83 ppm) < P–P (119–170 ppm) < P–Cl (216–269 ppm) < ( $\mu_{3}\text{P}$ )<sub>2</sub>(Fe(CO)<sub>3</sub>)<sub>3</sub> (14, 316 ppm) < ( $\mu_{3}\text{P}$ )(Fe(CO)<sub>3</sub>)<sub>3</sub> (13, 452 ppm). For phosphinidenes 13 and 14, the increasing number of electron withdrawing Fe(CO)<sub>3</sub> fragments and the P/Fe(CO)<sub>3</sub> ratio affects the chemical shift.

The 'closed' butterfly structure in **15–17** causes a high-field shift of the P–H and P–Cl resonances compared to 'open' **12 a**c, probably caused by an intramolecular transfer of electron density from the ferrocenyl core of the more rigid 1,1'substitution pattern.<sup>[10]</sup> The *endo*-P–P entities in **18**, **19** and **20** resonate at 119–170 ppm, which is significantly low-field shifted compared to alkyl-substituted [2]ferrocenophanes, that are observed at 21 ('Bu)<sup>[34]</sup> and 42 ppm (NEt<sub>2</sub>)<sup>[33a]</sup>. Compounds **19** and **20** exhibit two signals in their <sup>31</sup>P{<sup>1</sup>H} NMR spectra. Resonances of **19** appear down-field shifted by 41 and 51 ppm compared to **20**. The former exhibits a dd distribution pattern with large P,P coupling constants of 78 and 65 Hz. Instead, **20** solely couples as a doubled with  $J_{PP} = 21$  Hz, indicating different conformations of the involved structural motifs, particularly with a higher amount of *non*-periplanar orientations for **20**.

The analysis of compound **12** is more complex and requires a more detailed discussion. It was initially obtained as a mixture of six species, differing by the P-substitution pattern (**a**–**c**) as well as the configuration at the P atoms (*a*/*e*) (Scheme 2, Figure 2). Further chromatographic purification was complicated by the small amount of the mixture, the similar color, and behavior of the products. Nevertheless, further separation of the *a*,*a*-**12a** and *e*,*e*-**12a**, and *a*,*a*-**12b** mixture was achieved by column chromatography (Figure S6). Notably, monitoring via TLC is less indicative. Due to the overall low yield of these fractions, identification is focused to <sup>31</sup>P and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy (Figure 2).

In similarity to 11, where a mixture of both *a*-/*e*-isomers was observed, cluster 12a was identified in form of its isomers *a*,*a*:*a*,*e*:*e*,*e* in the ratio of 2.9:1.67:1 per P atom (Table S3), which reflects a similar preference towards the a-orientation compared to 11. Each isomer was assigned following the above described observation, where a-positioned groups R (herein, R=Fc) show their signals at higher fields.<sup>[37]</sup> Isomers a,a (247.4 ppm) and e,e (253.4 ppm) occurred as singlets; a,e-12a with signals at 245.3 (a) and 255.0 ppm (e) each with a  ${}^{2}J_{P,P}$ coupling constant of 109.1 Hz (Figure 2). Single Cl.H exchange resulted in compound 12b, which was formed as a, a and e, a isomers in a ratio of 8:1, based on integration of the PH signals in <sup>31</sup>P NMR spectra. The formation of the *e,e* isomer has not been observed since it could easily eliminate HCl<sup>[28c]</sup> and react further to 14. All PCI based signals are accompanied with a second set of signals, similar to 11, which is, however, not present for the PH signals. In case of a,a-12b it was unambiguously shown that these artifacts relate to the compound (Table S3), most probably caused by different orientations of the ferrocenyl group that solely impact PCI moieties. It should be noted that the a,a/e,e isomerization barrier for H-functionalized phosphido groups is comparably high and inversion was found to be absent at 100  $^{\circ}$ C for R=  $\mathsf{Ph}.^{^{[36]}}$  For sterically more crowded bis-(µ-PCIFc) derivatives, the obtained mixture is most probably kinetically controlled. The identity of a,a-12 a was additionally verified by single crystal Xray diffraction (Figure 3). Single crystals were obtained from the a,a-12a, e,e-12a, and a,a-12b mixture in which it appeared as the major product.

In addition to 12a and 12b, also 12c featuring two PH units was formed and observed as the *e,e*-isomer exclusively. In contrast to 12a, where the *a,a*-isomer is dominant (X = Cl), the *e,e*-product in 12c is most probably preferred, due to its lower steric demand in the axial position.<sup>[27]</sup> The assignment as *e,e* is in accordance with its <sup>31</sup>P{<sup>1</sup>H} NMR resonance signal, which appears as the most low-field shifted signal for PH fragments at 83.4 ppm compared to those where an *a*-configuration was assigned 12b (*a,a*: 72.3; *e,a*: 75.7 ppm).

For H containing **12b,c**, the <sup>31</sup>P NMR data exhibit <sup>1</sup> $J_{P,H}$  couplings of 404 Hz (*e*-PCl) and 387 Hz (*a*-PCl) for **12b** and 319 Hz for *e,e*-**12c**. Interestingly, the *anti*-periplanar orientation of the H atoms within *e,e*-**12c** results in a comparably high <sup>3</sup> $J_{P,H}$  coupling of 85 Hz, whereas an equatorial positioning of an H





**Figure 3.** ORTEP drawings of the molecular structures of *a*-11 (top, 30% probability level) and *a*,*a*-12a (bottom, 50% probability level) with their atom-numbering schemes. Hydrogen atoms are omitted for clarity. (Selected bond properties are summarized in Table 3.) Symmetry operation to generate equivalent atoms: (A) -x + 2, y, -z + 1/2.

atom (*i.e. a*-configuration) solely shows 23 (*e*,*a*-**12b**) and 8 Hz (*a*,*a*-**12b**).

An unusual effect occurs in the <sup>1</sup>H NMR spectrum of **15** and the <sup>31</sup>P NMR spectrum of *e*,*e*-**12**c, where an inverse 'roof'-effect for the PH hydrogen and phosphorous atoms can be observed (Figure S8).

The  ${}^{13}C{}^{1}H$  NMR signals of the carbonyl ligands are less indicative and are observed between 207.8 and 213.3 ppm.

The cluster cores can further be distinguished by IR spectroscopy, where  $\nu_{CO}$  stretching frequencies of terminal CO ligands are observed between 2080 to 1960 cm<sup>-1</sup>. The bridging carbonyl in compound **13** gave an additional band at 1809 cm<sup>-1</sup>, similar to Fe<sub>2</sub>(CO)<sub>9</sub> (1828 cm<sup>-1</sup>). For **11**, the carbonyls *anti* towards the electron-withdrawing Cl-bridge were found at highest energy (2078 cm<sup>-1</sup>).<sup>[37]</sup>

### Single-Crystal X-Ray Diffraction

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Single crystals of *a*-11, *a*,*a*-12 *a*, and 13–20 were obtained upon evaporation of dichloromethane solutions. Their ORTEP drawings are depicted in Figures 3–8, selected bond properties are



**Figure 4.** ORTEP drawings of the molecular structures of **13** (top, 30% probability level) and **14** (bottom, 50% probability level) with their atomnumbering schemes. Hydrogen atoms are omitted for clarity. Symmetry operation to generate equivalent atoms: (A) -x, y, z. (Selected bond properties are summarized in Table 2).

summarized in Tables 2 (phosphinidene clusters **13** and **14**) and 3. Although the structure of **14** has recently been described by our group,<sup>[16]</sup> it will briefly be discussed for comparison.

All herein described compounds crystallize in centrosymmetric space groups; in triclinic *P*-1 (**15-17**, **19**); monoclinic *P*2<sub>1</sub>/c (*a*-11), *P*2<sub>1</sub>/n (**13**), *C*2/c (*a*,*a*-12a, **20**); and orthorhombic *Cmc*2<sub>1</sub> (**14**). Compounds **17** and **19** contain two crystallographically independent entities in their asymmetric units. Compounds *a*,*a*-**12a**, **14**, **19** and **20** contain symmetry elements and show only half of molecule in the asymmetric unit.

A  $C_2$  axis in *a*,*a*-12a intersects the Fe–Fe bond perpendicularly. Cluster 14 contains a mirror plane generated by the Fe<sub>3</sub> motif. Compound 19 possesses an inversion center in the middle of the P–P bond, resulting in a *meso*-configuration  $(R_p, S_p)$ , whereas a  $C_2$  axis in 20 results in either a  $(S_p, S_p)$ - or  $(R_n, R_n)$ -configuration.

Compound **18** crystallizes in the *non*-centrosymmetric space group *P*-4*n*2 and the absolute configuration was established unambiguously (Flack x:  $0.021(10)^{[38]}$ ). A mirror plane is consequently absent. The tetragonal crystal system nevertheless

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Figure 5. ORTEPs (50% probability level) of the molecular structures of 15 (left), 16 (middle) and 17 (right) with their atom numbering schemes. C-bonded hydrogen atoms have been omitted for clarity. (Selected bond properties are summarized in Table 3).



**Figure 6.** ORTEP of the molecular structure of the organometallic octabisvalene **18**. (A) y + 1/2, x-1/2, -z + 1/2; (B) -x + 2, -y + 1, z; (C) 3/2-y, 3/2-x,  $\frac{1}{2}-z$ . (Selected bond properties are summarized in Table 3).





**Figure 8.** ORTEP (50% probability level) of the molecular structure of **20** shown in two different perspectives together with the atom numbering schemes. H atoms have been omitted for clarity. Symmetry operation for generating equivalent atoms: (A) -x, y, -z + 3/2.

structure is expanded by 3  $C_2$  axis that all cross in center of the  $P_4$  unit in a 90° angle. One intersects the Fe1–Fe1 bonds perpendicularly (B-labelled in Figure 6). A second one directs through both ferrocenyl's iron atoms, generating the A- and D-labelled parts. The third one proceeds perpendicularly with

**Figure 7.** ORTEP (25% probability level) of the molecular structure of **19** showing the atom numbering scheme of one of the two molecules in the asymmetric unit. H atoms have been omitted for clarity. Symmetry operation for generating equivalent atoms: (A) -x + 1, -y + 1, -z.

results in a highly symmetrical structure of **18**, showing only one quarter of the molecule in the asymmetric unit. The

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<b>Table 2.</b> Selected $(\mathring{A}/^{\circ})$ .	bond properties of phospl	hinidene clusters 13 and 14		
type	<b>13</b> (μ <sub>3</sub> -PFc)(Fe(CO) <sub>3</sub> ) <sub>3</sub> Bond distances [Å]	14 $(\mu_3\text{-PFc})_2(\text{Fe}(\text{CO})_3)_3$		
C-P	1.759(4)	1.791(3)		
Fe1–Fe2	2.7147(12)	2.6634(8)		
Fe1–Fe3	2.6648(11)	2.6657(8)		
Fe2–Fe3	2.6180(16)	3.5864(8) <sup>[a]</sup>		
P–Fe1	2.1026(13)	2.2095(8)		
P–Fe2	2.1595(14)	2.2643(9)		
P–Fe3	2.2194(14)	2.2282(9)		
P…P*		2.6027(14)		
$P_{0,0,0,}C_5H_4^{[b]}$	0.166(8)	0.124(5)		
Fe–Ct1	1.6403(9)	1.641(6)		
Fe–Ct2	1.6464(9)	1.653(6)		
	Angles and plane intersections [°]			
Ct1–Fe–Ct2	174.49(5)	176.17(10)		
$Fe_2P$ ···Fe_2P ( $\gamma$ ) <sup>[c]</sup>		10.35(3) <sup>e)</sup>		

[a] Symmetry generated; [b] P shift out of the cyclopentadienyl plane; [c] referring to the basal P<sub>2</sub>Fe<sub>2</sub> plane (Fe1 and Fe3).

regard to the  $P_4$  entity. The intersection of all three  $C_2$  axis also acts as an inversion center.

Compounds 13 and 14 possess *nido*-Fe<sub>3</sub>(CO)<sub>10</sub>( $\mu_3$ -PFc) and *nido*-Fe<sub>3</sub>(CO)<sub>0</sub>( $\mu_3$ -PFc)<sub>2</sub> cluster cores, respectively. Structure **13** (Figure 4) consists of a triangular Fe<sub>3</sub> plane which is  $\mu_3$ -bridged by a PFc phosphinidene fragment, similar to reported derivatives bearing alkyl<sup>[39]</sup> or aryl groups at P.<sup>[14]</sup> As expected, the shortest P-Fe bond is observed towards Fe1 (2.1026(13) Å), which is not involved in an additional  $\mu_2$ -CO bridging interaction. Hence, the interactions of P1 towards Fe2 (2.1595(14) Å) and Fe3 (2.2194(14) Å) are longer, but not symmetrical. The latter effect is compensated by a shift of the  $\mu_2$ -CO bridge towards Fe3 (C10-Fe3, 1.949(5) Å vs C10-Fe2, 2.056(5) Å). A further compensation of the weaker P-Fe3 donation occurs by a significant shortening of the Fe3-Fe1 bond (2.6648(11) Å) compared to Fe2-Fe1 of 2.7147(12) Å.

Compound 14 is best described as a distorted square pyramid, consisting of a tetragonal  $Fe_2P_2$  plane (rmsd = 0.0589) capped with a  $\mu_4$ -Fe(CO)<sub>3</sub> fragment in the axial position (Figure 4). The Fe–Fe distances of 2.6634(8) and 2.6657(8) Å are comparable with the Fe1–Fe3 bond in 13. The P-P interaction of 2.6027(14) Å was found to play a non-negligible role and even shortens upon reduction of the cluster.<sup>[16]</sup> The non-binding Fe1...Fe3 interaction is 3.5864(8) Å. Based on the geometry of the core, the shortest P-Fe distances are found towards the basal Fe atoms (2.2094(8)/2.2282(9) Å) and an increased value towards Fe2 of 2.2643(9) Å.[16]

Compounds a-11, a,a-12a, and 15-20 contain a Fe<sub>2</sub>(CO)<sub>6</sub>based butterfly motif. It is generally coordinated by 2 PFc ligands, except for a-11 and 20 in which one PFc moiety is replaced by a  $\mu_2\text{-}\text{Cl}$  and a  $P_2$  entity, respectively. Within the latter a 'classic' PFe<sub>2</sub>(CO)<sub>6</sub> and an 'unusual' P<sub>2</sub>Fe(CO)<sub>4</sub> fragment are combined wherefore the structure cannot be described by the classic butterfly parameters (see below and Figure S3, Figure S4).

The butterfly entity in compounds a-11, a,a-12a can be considered as 'open', meaning that the P donor atoms belong to individual ligands. Hence, each of these ligands coordinates in a  $\mu'_{,\kappa}$  fashion. The 1,1'-ferrocenediyl backbone in 15–17 instead, coordinates in a  $\mu',\kappa^4$  motif, resulting in a 'closed' butterfly.

The description of compound 18 is more complicated. The P ligands within one Fe<sub>2</sub>(CO)<sub>6</sub> motif belong to different ferrocenyls ( $2 \times \mu', \kappa^2$ ). However, each sandwich fragment coordinates to two butterfly entities  $(\mu,\mu',\kappa^4)$ , resulting in a macrocyclic assembly, known as organometallic octabisvalene, i.e. bis (hexacarbonyl-(µ<sub>2</sub>-diaryldiphosphene)di-iron). Such structures are rare and have solely been reported for two derivatives so far, in which four methyl,<sup>[32,40]</sup> or two  $\mu_2$ -bridging Fe(CO)<sub>4</sub> fragments<sup>[2]</sup> replace the two *ansa*-ferrocenyls. One structural feature of these diphosphenes is a P-P bond, which is established between the 1,1'-substituents resulting in a 2,3diphospha[2]ferrocenophane motif. In compounds 19 and 20 the P-P bond is observed between two individual ferrocenyls, since the increased P-P distance of the 1,2-substitution pattern prevents an intramolecular P–P bond. The resulting tetraphosphido ligand exhibits a  $\mu,\mu',\kappa^8$  coordination of the whole fragment, or a bis( $\mu,\kappa^4$ ) mode if the ligand is considered as a dimer of two motifs. The latter formalism better represents the symmetry within the solid state structures and allows for an easier assignment via the  $\kappa$ -nomenclature, resulting in a bis  $(1\kappa^2 P^1, P^{2'}-2\kappa^2 P^1, P^{2'})$  coordination mode for **19** and bis $(1\kappa^2 P^1, P^{2'} 2\kappa^2 P^1$ ,  $P^2$ ) for **20**. Thus, the butterfly fragments in **19** are exclusively connected by P atoms from different ferrocenes ( $\mu$ ), whereas the ortho-P atoms in 20 chelate to one iron carbonyl moiety ( $\mu$ '). The different connectivity mode results in a rather flat geometry for 19 and a pocket-type shape for 20. As a further main difference between both structures, the conformation regarding the central P-P bond needs to be mentioned. In case of 19, the inversion center, positioned in the P-P bond, results in an ideal anti-periplanar orientation of bonds to symmetry generated atoms. The smallest (synclinal) angles are observed for the C7-P1-P1A-Fe2A torsion of 34.9(4)°.[41] For 20, the P–P bond intersects a perpendicular  $C_2$  axis, resulting in torsion angles to equal atoms of 34.5(2) (C11), 114.12(5) (Fe2) and 157.09(5) (Fe1). The smallest torsion is observed for Fe1–P2A–P2–Fe2 of only 21.5(2)°, due to the  $\mu' \kappa^2$  coordination of the  $P_2$  entity towards a  $Fe_2(CO)_6$  fragment. The difference of the syn-/anti-periplanar conformation is also reflected in the different coupling pattern of **19** (dd) and **20** (d) in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra (see above).

The P-bonded ferrocenyl groups are predominantly found in the axial (a-) positions regarding the butterfly motif, due to structural requirements (15-17) or a kinetic preference (a-11 and a,a-12, see above). Equatorially (e-) positioned ferrocenyls are only found in 18 and 19, containing P-P bonds as exosubstituents.

For the 'normal'  $X_2 Fe_2(CO)_6$  (X = P, CI) butterfly structures a-11, a,a-12 and 15–19 a rather symmetrical coordination of the P,X donors towards the iron atoms can be observed. The highest deviation within a  $Fe_2-\mu_2-X$  coordination entity is observed for a,a-12 a with 0.041 Å. Fe–Cl bonds are with 2.30 Å enlarged compared to Fe-P bonds (~2.20 Å). Longer P-Fe distances are only observed for the P<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> pattern in 20



(2.2957(10) and 2.3541(10) Å), in which the bridging P atoms coordinate towards two *trans*-positioned  $Fe(CO)_3$  motifs instead of one *cis*-Fe<sub>2</sub>(CO)<sub>6</sub> building block.

Although the P–Fe distances are constant throughout the series of compounds (~2.21 Å), the Fe-Fe distance of the Fe<sub>2</sub>(CO)<sub>6</sub> motif spans from 2.55 to 2.77 Å (Table 3). A CSD search revealed that an Fe-Fe distance of ~2.62 Å (MEDIAN of 84 CSD entries) is most common, which is close to the values observed for closed 15–17. Increase of the opening angle as found in a,a-12 increases the Fe-Fe bond length to 2.6955(8) Å, whereas a reduced P-P distance decreased the bond length to 2.6098(9) Å. It should however be noted that within the series of 15-17 a steady reduction of the P-P distance is not reflected in the accompanied Fe-Fe bond distance. Hence, the nature and electronic properties of the bridging ligands seem to be decisive as found in a-11. Therein, replacement of one PFcCl by a CI group reduces the Fe-Fe distance to 2.55 Å, due to the longer Fe--Cl interaction compared to Fe--P. The significantly smaller Fe–Fe bond length in 18 is thus better explained by the different electronic nature of the P-P entity compared to a P-CI or P–H functionality.

The P-P distance between both phosphorous donor atoms of ~2.78 Å herein (Table 3), is similar to clusters bearing other bridging groups including flexible (e.g. alkyl), and rigid (e.g. 1,8-naphthalenyl) fragments.<sup>[33b,42]</sup> The P-P interaction of ~2.8 Å seems to be ideal (Figure S4) since non-bridged butterfly structures such as a-11 and a,a-12a adopt similar values (Table 3). Furthermore, the 1,8-C-C distance in rigid 1,8naphthalenyl fragments, which should ideally be equal to the P-P separation in the respective bisphosphine ligand, is increased from ~2.50 Å<sup>[43]</sup> to 2.74 Å.<sup>[42]</sup> Other rigid bisphosphinyl motifs, such as biphenylene (C--C ~ 3.65 Å),[27] xanthene (C--C ~4.3-4.8 Å)<sup>[44]</sup>, and [2.2]paracyclophane (C.-C 3.1-3.5 Å)<sup>[45]</sup> have so far not been used in metal carbonyl cluster chemistry, wherefore comparison is limited to the mentioned examples above. Herein, the P-P distance reaches its maximum for a,a-12 a (2.8848(15) Å), most probably due to an electronic repulsion of the  $\pi$ -systems of both ferrocenyls. The repulsion also results in a bending of the C5H4 plane out of an ideal axial orientation by 13.53(10)° (Table 3). Contrary, a-11 is only bent by 2.13(13)°. Besides these differences compounds a-11 and  $a_1a$ -12a show structurally similar butterfly cores with Fe<sub>2</sub>P...PFe<sub>2</sub> opening angles ( $\gamma$ ) of 100.49(4)° and 111.66(3)°, respectively. Both structures have been superimposed for a better visualization of their geometrical differences/similarities (Figure S5).

For closed butterfly structures **15–17** and [2]ferrocenophane **18** the P…P distance (~2.8 Å) is below the size of the ferrocenyl backbone (~3.3 Å). The shortening of the P…P distance is interestingly not compensated by a decrease of the Ct–Fe–Ct tilt angle  $\delta$  of the ferrocenylene entity. Instead, the shift of the P atom out of the adjacent C<sub>5</sub>H<sub>4</sub> plane increases via 0.003(7) (*a*-**11**) < 0.059(5) (*a*,*a*-**12 a**) < 0.081(5) (**15**) < 0.092(13)/0.118(13) (**16**) < 0.132(6)/0.173(6) (**17**) < 0.254(5) Å (**18**).

Due to the 1,2-substitution pattern in **19** and **20** their o.o.p. shift depends on whether the respective P atom is located outside ( $P^{CI}$  entity) or the inside ( $P^{P}$ ) of the assembly, as well as of structural differences between **19** and **20**.

Both compounds feature coplanar  $C_5H_3$  planes (**19**, 0.0(7); **20**, 6.29(16)°) and {Fe( $\eta^5$ - $C_5H_5$ )} entities directing to opposite directions. In case of **19**, the distance between these planes is 1.23(10)/1.00(11) Å, which is compensated by o.o.p. shifts of the P atoms by 0.445(17) and 0.34(2) Å for the central P<sup>P</sup>, and 0.043(17)/0.008(18) Å for the outer P<sup>CI</sup> atoms. The different o.o.p. shifts assemble the four P atoms in an ideal plane (rmsd = 0), which intersects the adjacent cyclopentadienyls by 17.7(5) and 16.0(4)°. The *trans*-directing CI atoms are positioned within the P<sub>4</sub> plane (0.001(7)/0.054(7) Å).

Within the pocket-type structure of **20** (Figure 8 and Figure 9) the C<sub>5</sub>H<sub>3</sub> entities of both ferrocenes are facing each other, resulting in a strong intramolecular parallel displaced  $\pi$ - $\pi$  interaction between the C<sub>5</sub>H<sub>3</sub> rings of both organometallics of 3.327(2) Å with a slippage of ~1.2 Å ( $\alpha$ <sub>C5H3-C5H3</sub>=6.29(16)°). The shortest distance can be found between C10 and the centroid of the opposite C<sub>5</sub>H<sub>3</sub> plane (d=3.124(3) Å). This repulsion might cause the large bending of both P atoms out of the C<sub>5</sub>H<sub>3</sub> planarity by 0.261(6) (P<sup>CI</sup>) and 0.361(6) Å (P<sup>P</sup>).

Another important parameter to particularly describe [2] ferrocenophanes is  $\tau$  (Table 3). It describes the torsion angles of the P–P bond with regard to the ferrocenyl axis. For comparison,  $\tau$  does not exceed 3.34(3)° in **15–17**. [2]Ferrocenophane **18** shows a slightly increased value of 8.98(4)°, which is the second lowest twist parameter ( $\tau$ )<sup>[34]</sup> reported so far. Usually, values of up to 43.2° are typical.<sup>[33a]</sup> Herein, the system escapes the tension with a reduced Fe–Ct distance of solely 1.6285(1) Å. A further tilting occurs in the central P<sub>4</sub> unit of **18**. The distorted rectangle with distances of 2.2459(14) (P–P) and 2.7550(11) Å (P…P) is twisted by 17.40(8)°. This also causes a torsion of both Fe<sub>2</sub>(CO)<sub>6</sub> groups by 16.71(4)° towards each other. For the whole molecule a twist angle of 35.31(9)° can be observed.

The unusual Fe<sub>2</sub>P<sub>3</sub> coordination mode in **20**, which is the second example of an iron carbonyl butterfly structure involving three different donor atoms so far,<sup>[46]</sup> does not exhibit the typical butterfly structure, wherefore a plane intersection between both wings cannot easily be defined. The description is complicated by the fact that the central P<sub>2</sub>Fe<sub>2</sub> coordination fragments are not planar (rmsd = 0.1895, Figure 9). The tetragon is of an irregular shape, not only due to the differences between P–P (2.1853(18) Å) and Fe–Fe (2.7775(7) Å) bonds, but also varying Fe–P coordination distances (Fe2–P2, 2.3541(10); Fe1–P2 A, 2.2957(10) Å). The Fe-P distances towards the



Figure 9. Ball-and-Stick representation of 19 (left) and 20 (right). The iron carbonyl coordination spheres are highlighted for comparison.

Table 3. Selected bond p	roperties of butterfly	-type (BF) compou	unds <i>a</i> -11, <i>a</i> , <i>a</i> -12 <b>a</b> and	15–20 (Å/°) based on thei	r single crystal X-ray diffraction	n analyses. <sup>[a]</sup>		
	<i>a</i> -11	a,a- <b>12a</b>	15	16	17	18	19	20
BF hetero atoms BF structure (P)R <sup>eco</sup> butterhy (P)R <sup>endo</sup> butterhy (P)R <sup>endo</sup> butterhy	P,Cl open Cl Fc	P,P open CI Fc	P,P 1,1'-bridged H Fc	P,P 1,1'-bridged H,Cl Fc	P,P 1,1'-bridged CI Fc	P,P open/ansa Fc P	P,P open a: Cl; b: Fc a: Fc; b: P	P,P <sub>2</sub> 1,2-bridged a: Cl; b: Fe(CO) <sub>3</sub> a: Fc; b: Fc
bond distances/A PP <sub>P2Fe2(CO)6</sub>	2.8507(14) <sup>9)</sup>	2.8848(15)	2.8257(10)	2.807(3)	2.7721(13) 2.7674(12)	2.7550(11)	2.798(4) 2.802(5)	2.9149(12) 3.1657(13)
PP <sub>ortho</sub> CP	1.779(4)	1.784(3)	1.797(3) 1.700(3)	1.752(7)	1.779(4)-	1.814(3)	3.594(4)-3.581(4) 1.786(7)-1.775(7) <sup>CI</sup> 1.050/6) 1.0770(P	2.9149(12) 1.777(3) <sup>Cl</sup> 1.816(2) <sup>P</sup>
P_R <sup>exo</sup>	2.0394(14)	2.0703(11)	1.798(3) 1.32(3) 1.33(3)	1.701(8) 1.36(7) (H) 2.047(3) (CI)	1.780(4) 2.0750(12)–2.0817(12)	= P-Fe	1.838(0)-1.837(8) 2.015(5)-2.029(5) <sup>CI</sup>	1.810(3) 2.0548(13) <sup>CI</sup>
P_P						2.2459(14)	2.232(6)-2.231(5)	2.1853(18)
Fe-CI	2.1946(12) 2.2091(11) 2.3026(12)	2.1831(9) 2.1831(9)	2.2149(8) 2.2149(8)	2.211(2) 2.211(2)	2.1934(10)- 2.2122(10)	2.2374(9)	P <sup>-1</sup> : 2.130(4)/2.173(4) P <sup>0</sup> : 2.238(3)/2.255(4)	2.2957(10)/2.3541(10)
Fe-Fe Ct-Fe (Ct1)	2.5541(9) 1.6420(7)	2.6955(8) 1 6334(4)	2.6393(6) 1 6430(4)	2.6349(15) 1 6430(12)	2.6467(7), 2.6394(7) 1 6414(5)- 1 6427(5)	2.6098(9) 1.6285(1)	2.662(2)-2.650(2) 1 6297(18)-1 630(2)	2.7775(7) 1.6459(5)
(Ct2)	1.6532(6)	1.6496(4)	1.6454(4)	1.6424(12)		(1)0070.1	1.6621(18)-1.6513(19)	1.6612(5)
P <sub>0.0.p</sub> C <sub>5</sub> H <sub>4/3</sub> <sup>[d]</sup>	0.003(7)	0.059(5)	0.081(5)	0.092(13)-0.118(13)	0.132(6)-	0.254(5)	P <sup>CI</sup> : 0.043(17)–0.008(18) D <sup>P</sup> . 0.445(17) 0.34(2)	P <sup>CI</sup> : 0.261(6) D <sup>P</sup> . 0.361(6)
C <sub>5</sub> H <sub>3</sub> C <sub>5</sub> H <sub>3</sub>			(c)+/0.0		(0)671.0		1.23(10)-1.00(11) <sup>[]]</sup>	3.124(3) <sup>[k]</sup>
Angles and plane	intersections /°							
Ct-Fe-Ct (ð)	177.67(4)	177.52(3)	177.4(3)	178.84(7)	179.80(4)	174.23(4)	174.59(11)–172.73(16)	174.55(3)
$Fe_2P$ - $Fe_2P(\gamma)$	100.49(4) <sup>[g]</sup>	111.66(3)	105.36(3)	105.04(7)	1/ 0.0/ (4) 103.69(3) 103.25(2)	100.17(2)	104.79(12)	81.79(3) <sup>P2,[1]</sup>
$\begin{array}{c} C_5 H_{4/3} C_5 H_{4/3} & {}^{inter \ Fc} \\ C_5 H_{4/3} C_5 H_{4/3} & {}^{intra \ Fc} & (\alpha) \end{array}$		19.01(17) 2.0(2)	5.8(3)	5.1(6)	(c)cc.co1 3.73(17)	35.31(9) 9.99(14)	0.0(7) 0.0(7) 5.6(6)	6.29(16) 6.29(16) 5.28(17)
CtCP ([3) <sup>[e]</sup>		1.4(2)	2.4(2)	3.0(6)-	4.67(19) 5.0(3)-	7.8(2)	8.9(4) a: -2.6(7),(-)0.3(9)	a: -15.3(3)
			2.6(2)	3.5(6)	4.1(3)		b: -14.5(6),M- > 11.0(7)	b: -16.0(3)
P <sup>REXO_</sup> P_R <sup>Endo</sup> ( <i>f</i> )	92.13(13) <sup>[g,h]</sup>	99.04(10) 103.53(10) <sup>[1]</sup>	95.44(9)/95.33(9)	99.8(3) (T) 95.4(3) <sup>4</sup> 96.4(3) <sup>4</sup>	96.17(11)- 99.45(12) 96.25(11)- 97.21(11)	101,943(10) 121.16(11) 102.40(10)	– a: 92.50(18),92.4(3) b: 90.50(18),90.0(2)	- a: 64.71(11),67.06(11) b: 98(11),83.61(12)
Torsion angles $/^{\circ}$ R <sup>eve</sup> -PP $-R^{evo}$ Ct $-PP-Ct$ ( $r$ )		25.0(3)	6(6) 0.62(2)	6(8) 0.44(6)	1.3(4) 3.34(3)- 0.01(3)	17.40(8) 8.98(4)	13.2(17),12(5)	n.a.
С-Р-Р-С РРРР Fe14 <sup>II</sup>						16.71(4)	180.0(0) 180.0(0)	34.5(2) 155.26(5)
[a] n.a. = not applicable; tl the C <sub>5</sub> H <sub>43</sub> plane, <i>γ</i> : openir Fe1-labeled atoms are rep P-substituent; d) distance present; [h] ClP-C bonc intramolecular parallel-dis	he defined parameter ng angle of the butte orted first; in case of of the P atom shifteo J, [I] A PP bond is placed $\pi$ $\pi$ interacti	s $\alpha, \beta, \gamma, \delta, \theta, \tau$ all which motif, $\delta$ bend with motif, $\delta$ bend a 1,1'-substitution a 1,1'-substitution J out of the $C_5H_4$ present; [J] The $c_5H_4$ present; [J] The $c_5H_4$ present; [J] The $c_5H_4$ present for $M$ and	low for a comparison w ling of the ferrocenyl bi pattern the assignmen blane; [e] Negative valuu distances between two slippage of $\sim 1.2$ Å; [1] S	ith literature reported [2]f ackbone, <i>θ</i> : inner P-angle, it as Ct1/2 follows an incre, es represent a positioning es represent a positioning mean square planes gen ée description in the text	errocenophanes <sup>33,</sup> $\alpha$ = openin $\pi$ : ferrocenyl/P–P to:, $Ct$ = asing atom labeling; [b] P-subs above the plane; [f] Torsion b above the plane; [f] Torsion b nerated through both $C_5H_3$ e i and Figures 7–9.	g angle of the fe Centroid of the i tituent directing etween the opp ntities is given;	performed in the sector of the sector of the sector of $C_5H_{4,3}$ (1) and $C_5H_{5,4}$ (2) groups in the reaction of the $Fe_2(CO)_6$ environment of the sector of the	g of the P atom out of s; Interactions towards ntity; [c] <i>endo</i> -directing stead of P a Cl atom is given, representing an

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opposite corners of 3.4541(10) Å (Fe1...P2) and 3.2277(10) Å (Fe2-P2 A) should not be considered as binding interactions. However, they divide the tetragon into two possible sets of  $P_2Fe$  and  $PFe_2$  triangles, whose plane intersections of 25.26(3)° (shorter, Fe2-P2A hypotenuse) and 27.24(3)° (longer, Fe1-P2 hypotenuse) give a better expression of the shape of this fragment. Reconsidering the bend angle of the butterfly structure, values of 81.79(3)°, including the ortho P atom, and 98.67(3)° with P2 A are observed. Compound 19 exhibits plane intersections of ~104.5°, which is similar to those of 15-17(Table 3).

The either flat (19) or pocket-type (20) geometry significantly affects the P-P distance between the ortho-positioned P atoms. The former shows values of 3.594(4)/3.581(4) Å, which is close to an ideal value of 3.513(3)-3.603(6) Å (Table S2). For compound 20 the proximity between both ortho phosphorous atoms is reduced to 2.9149(12) Å, which is below the smallest so far reported value of 2.950(7) Å for a NiCl<sub>2</sub> complex coordinated by two PPh<sub>2</sub> groups.<sup>[47]</sup> In **20** both C–P bonds are similarly bended away from an ideal C-C-P angle of 126° to 113.1(2)/115.1(2)°, due to a coordination towards the same Fe atom, requiring a closer proximity. For 19 instead, the ortho-P atoms bind to Fe atoms ( $\mu$ ) of the two *trans*-positioned Fe<sub>2</sub>(CO)<sub>6</sub> fragments (Figure 7 and Figure 9). The C-P distances follow the trend where C-P<sup>CI</sup> distances are significantly shorter by at least



Potential in V vs FcH/FcH<sup>4</sup>

Figure 10. CV of 14 in dichloromethane solutions (1.0 mmol L<sup>-1</sup>) at 25 °C measured with a glassy carbon working electrode. Supporting electrolyte 0.1 mol L<sup>-1</sup> of  $[N^n Bu_4][B(C_6 F_5)_4]$ ).

Table 4. Cyclic voltammetry data (in mV) of 11, 13, 14, and 17. <sup>[a]</sup>					
Compd.	$E^{\circ'}$ <sup>[b]</sup> $(\Delta E_{\rm p})^{\rm [c]}$	$\Delta E^{\circ'[d]}$			
11 13 14 <sup>(f)</sup> 17	327 (85) 346 <sup>[e]</sup> 295 (62) 465 (63) -1605 (68) -1755 (64) 650 (99)	- - 170 150			

[a] Potentials vs FcH/FcH<sup>+</sup>, scan rate 100 mV s<sup>-1</sup> at a glassy-carbon electrode of 1.0 mmol L<sup>-1</sup> solutions in anhydrous dichloromethane containing 0.1 mol  $L^{-1}$  of  $[N^n Bu_4][B(C_6 F_5)_4]$  as supporting electrolyte at 25 °C. [b] Formal potential. [c] Difference between the cathodic and anodic peak potential. [d] Potential difference between the first and the second redox processes. [e] Obtained from SWV measurements. [f] Derived from reference 16. [g] Irreversible; cathodic peak potential.

0.052 (19) and 0.080 Å (20) (Table 3) compared to those of  $C{-}P^{^{P}}$ bonds, which is also observed for 15-17 (see above).

## (Spectro)Electro Chemistry

The electrochemical behavior of 11, 13,  $14^{[16]}$  and 17 were investigated by cyclic voltammetry (CV) and square-wave voltammetry (SWV) (Figure 10 and Figure S9). The electrochemical measurements were performed in anhydrous dichloromethane solutions under inert conditions containing [N<sup>n</sup>Bu<sub>4</sub>][B- $(C_6F_5)_4$ ] (0.1 mol L<sup>-1</sup>) as supporting electrolyte, which stabilizes highly charged species and minimizes ion pairing effects (Experimental Part).<sup>[48-51]</sup> The redox potentials are summarized in Table 4. Compounds 11, 14 and 17 show reversible oneelectron processes of which four are present well-separated for 14. Cluster 13 instead exhibits several irreversible processes, indicating decomposition under the conditions applied (Figure S9). The only observable redox process for 11 ( $E^{\circ\prime} = 327 \text{ mV}$ ) is related to the ferrocenyl group, indicating that the {Fe<sub>2</sub>(CO)<sub>6</sub>(µ-Cl)P} fragment is redox inactive in the electrochemical window applied. Cluster 14 showed both ferrocenylrelated redox processes at 295 and 465 mV as well-separated processes with a redox separation of 170 mV. This separation is based on electrostatic interactions, since IVCT bands were not observed in the NIR region.<sup>[16]</sup> Comparison of the E<sup>a</sup>/E<sup>c</sup> difference for 11 and 14 reveals a slightly broadened signal for the former, which is most probably caused by the presence of a mixture of a- and e-isomers. Compound 17 shows the most cathodically-shifted redox process (650 mV), due to the highly electron withdrawing effect of the  $Fe_2(CO)_6$  fragment. The reduction of the latter could be observed at -1883 mV as an irreversible process. Nido cluster 13 also showed a lessreversible redox behavior under cathodic conditions, contrary to nido cluster 14, which underwent two well-separated reduction processes (-1605 and -1755 mV), based on a reduction of the  $Fe_3(CO)_9P_2$  core. Therein, a radical anion is formed initially, which is equally distributed within the core, proven by in situ EPR measurements and DFT calculations.<sup>[16]</sup> Further reduction of [14]<sup>•-</sup> formed the diamagnetic anionic cluster [14]<sup>2-</sup>.

The redox potentials of the cluster core reflect the electronic properties of the P-bonded groups, as shown recently.<sup>[52]</sup> Comparison with the values therein reveals that the ferrocenyl group in 14 (-1605 and -1755 mV) possesses electron donating properties similar to those of strongly electrondonating p-OMe (-1530 and -1760 mV) and p-NMe<sub>2</sub> (-1630 and -1790 mV) groups attached at the Ph-functionalized Fe<sub>3</sub>(CO)<sub>9</sub>P<sub>2</sub> cluster cores.<sup>[3]</sup>

The reversible redox behavior of 14<sup>[16,53,54]</sup> under electrochemical conditions allowed for further spectro-electrochemical IR measurements, where the shift of the  $\nu_{\rm CO}$  stretching frequencies should reflect the charge distribution upon oxidation and reduction (Figure 11 and Table 5). Upon single and double oxidation to [14]<sup>+</sup> and [14]<sup>2+</sup>, respectively, a hypsochromic shift of all bands by ~ 10 cm<sup>-1</sup> occurs. The band distribution for 14 and  $[14]^{2+}$  is similar, indicating that the overall geometry



**Figure 11.** *In situ* IR spectra of **14** (left) and **17** (right) at 25 °C in dichloromethane (2 mmol L<sup>-1</sup>) at rising (top) and decreasing potentials (bottom) *vs.* Ag/AgCl. Supporting electrolyte 0.1 mol L<sup>-1</sup> of [N<sup>o</sup>Bu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]; Pt working electrode.

Table 5. Selected IR data of the carbonyl regions of 14 and 17 upon reduction and oxidation. $^{\rm (a)}$					
$\Delta  u_{ m red}$	[14] <sup>-</sup>	14	<b>[14]</b> <sup>+</sup>	<b>[14]</b> <sup>2+</sup>	$\Delta v_{ m ox}$
	-	2065	2075	2085	10/10
49	1986	2035	2046	2056	10/10
			2035	2036	
42	1971	2013	2027		
			2013	2013	
59	1935	1994	1998		
$\Delta v_{\rm red}$	[17]-	17	[ <b>17</b> ] <sup>+</sup>		$\Delta v_{ox}$
		2073	2089		16
51	1985	2036	2053		17
60	1955	2015			
58	1929	1987			
[a] All values are given in cm <sup>-1</sup> .					

remains comparable. In case of  $[14]^+$  a mixed pattern is observed, representing a less symmetrical species, based on oxidation states, excluding communication in this mixed-valent species. That electrostatic interactions of distant, non-conjugated redox-active groups can affect the value of the respective CO stretching frequencies was recently shown for a Fe<sub>2</sub>(CO)<sub>6</sub>( $\mu_3$ -PR)<sub>2</sub> butterfly species (R=CH<sub>2</sub>Fc).<sup>[14]</sup> The congested bridged butterfly species **17**, showing a reversible ferrocenyl- and an irreversible core-based redox event, was investigated for comparison (Figure 11, Table 5). Upon stepwise oxidation of **17** to [**17**]<sup>+</sup> only minor changes of its IR spectra occurred in which the intensity of all four bands decreased slightly and two weak bands rose at higher wavenumbers. Assuming that they are related to the intense adjacent vibrations, a shift  $\Delta v_{ox}$  of 17 and 16 cm<sup>-1</sup> occurs, which is similar to **14**.

Although our measurement conditions did not allow for a further increase of the potential it can be assumed that oxidation was close to completeness at 1700 mV (vs Ag/AgCl). For comparison, formation of  $[14]^{2+}$  was almost finished at 1100 mV (Figure S10). Together with the redox potentials for  $[14]^{+}/[14]^{2+}$  (465 mV vs FcH/FcH<sup>+</sup>) and 17/[17]<sup>+</sup> (650 mV), that differ by 185 mV, formation of 17 should be finished before a

potential of 1700 mV is reached. This in turn shows that oxidation of the ferrocenylene backbone causes only minor changes within the symmetry of the compound and the energy of the carbonyl stretching.

The reduction of 14 resulted in a bathochromic shift ( $\Delta v$ ) of the carbonyl stretching frequencies by ~50 cm<sup>-1</sup> towards [14]<sup>-</sup> (Table 5), showing an increased impact of a single charge compared to a  $\Delta v$  of 10 cm<sup>-1</sup> for the 14/[14]<sup>+</sup> and [14]<sup>+</sup>/[14]<sup>2+</sup> transitions upon oxidation. This verifies that reduction occurs within the Fe<sub>2</sub>(CO)<sub>9</sub>P<sub>2</sub> core, directly affecting the coordinating carbonyls. However, the steady conditions within the used OTTLE (=optically transparent thin layer electrochemical) cell resulted in a rapid decomposition of [14]<sup>2-</sup> upon steady exposure to the negative potentials.<sup>[16]</sup>

Reduction of **17** and formation of  $[17]^-$  reduced the intensity of three of the four stretching frequencies and gave rise to two new bands at lower wavenumbers (Table 5). The equal intensity of the stretching at 1987 cm<sup>-1</sup> indicates that vanishing and growth of bands occurred simultaneously. The three bands of lowest energy seem to correspond to each other, due to their similar intensity distribution and separation. Thus, a bathochromic shift of ~55 cm<sup>-1</sup> occurs upon reduction, which is similar to **14** (~50 cm<sup>-1</sup>). This confirms that reduction occurs at the Fe<sub>2</sub>(CO)<sub>6</sub>P<sub>2</sub> fragment. The slightly larger shifts for the oxidation and reduction processes of **17** can be explained with the smaller number of Fe(CO)<sub>3</sub> fragments compared to **14**. For the latter, negative and positive charges are distributed over three Fe(CO)<sub>3</sub> cores, contrary to **17** with just two metal carbonyl fragments.

#### **Computational Methods**

Recent investigations of nido-cluster 14 showed that its reversible redox processes in the anodic and cathodic region can be explained with ferrocenyl-based HOMO and core-based LUMO orbitals.<sup>[16]</sup> A cobalt derivative instead revealed corebased HOMO orbitals, resulting in non-reversible redox processes.<sup>[16]</sup> Similar differences are observed for  $\mu_2$ -Cl-bridged butterfly compound a-11 and the pyramidal nido-Fe<sub>3</sub>(CO)<sub>10</sub>( $\mu_3$ -PFc) phosphinidene cluster 13. The former gave one reversible Fc/Fc<sup>+</sup>-related redox process (Figure 10), whereas 13 showed an irreversible behavior and SWV measurements were required (Figure S9). Hence, DFT calculations were carried out for a-11 and 13 to prove if this behavior can be correlated with the location of HOMO and LUMO orbitals (Figure 12). Indeed, whereas the LUMO is localized at the metal carbonyl units for both compounds, the location of the HOMO differs. In agreement with the reversible redox behavior of 11 in CV experiments, its HOMO with the energy of -6.384 eV is found to be ferrocenyl-based.

At the same level of theory, the HOMO of the neat ferrocene is predicted at -5.855 eV. Stabilization of the Fc-based orbital in **13** by 0.529 eV agrees with its considerably more positive oxidation potential when compared to the unsubstituted FcH/ FcH<sup>+</sup> redox pair (note that the measured redox potential also





**Figure 12.** DFT-calculated energies and isosurfaces of the HOMO and LUMO orbitals of *a*-**11** (left) and **13** (right). Theory level: ZORA-PBE0-D3BJ/def2-TZVPP(SARC).

includes contribution from solvation energy and hence should not be equal to the difference of Fc-based MO energies).

The HOMO of **13** with the energy of -6.467 eV is localized on the metalcarbonyl cluster core, which explains the irreversible redox behavior of **13** in the anodic range. The ferrocenylbased MO in **13** is the HOMO-2 with the energy of -6.671 eV, 0.204 eV below the HOMO of **13** and 0.816 eV below the HOMO of Fc.

# Conclusion

The reaction of the PCl<sub>2</sub>-functionalized ferrocenes Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>PCl<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) (5), Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>PCl<sub>2</sub>)<sub>2</sub> (6) and Fe( $\eta^5$ -C<sub>5</sub>H<sub>3</sub>-1,2-(PCl<sub>2</sub>)<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) (9) with Fe<sub>2</sub>(CO)<sub>9</sub> is reported, resulting in the formation of various single- and double-ferrocenyl-functionalized clusters. All dichlorophosphines were obtained upon reaction of their PH<sub>2</sub> species with a toluene phosgene solution, a new approach for the latter two substrates.

The main structural feature of the clusters obtained is a  $Fe_2(CO)_2(\mu_2-PFc)_2$  butterfly entity, whereas **5** gave *open* and **6** *closed* motifs, with the ferrocenediyl building block bridging both P donor atoms. The *open* butterfly structures were obtained with different configurations of the PFc groups with regard to the V-shaped  $P_2Fe_2(CO)_6$  building block were observed, whereby an axial (*a*-) positioning was preferred in both cases. Dichlorophosphine **5** additionally gave phosphinidene clusters of type *nido*-Fe<sub>3</sub>(CO)<sub>10</sub>( $\mu_3$ -PFc) (**13**) and bipyramidal *nido*-Fe<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ -PFc)\_2 (**14**).

In addition to the *closed* butterfly structures in which the 1,1'-ferrocenediyl backbone adopts a  $\mu', \kappa^4$ -binding mode, a further example of an organometallic octabisvalene was formed. Therein, a direct P–P bond between both cyclopentadienyls results in a [2]ferrocenophane motif, coordinating towards two *exo*-directing iron carbonyl fragments in  $\mu_{2r}\mu',\kappa^4$ 

binding modes. The reaction of **9** with homoleptic metal carbonyls resulted in two isomers consisting of a P–P connected dimer, which coordinates towards two independent Fe<sub>2</sub>(CO)<sub>6</sub> fragments in a novel  $\mu,\mu',\kappa^8$  or bis( $\mu,\kappa^4$ ) fashion. Both structures vary in their binding modes of the *ortho* P atoms towards the Fe<sub>2</sub>(CO)<sub>6</sub> entities. Compound **19** reveals  $\mu$ -interactions towards iron atoms of different metal carbonyl fragments exclusively. For **20** instead,  $\mu,\mu'$  motifs as well as coordination towards same iron atoms occur. The different coordination modes cause a flat and a pocket-type shape, respectively. The chelating coordination mode in **20** also requires a bent of both *ortho* P atoms towards each other, resulting in the shortest so far observed P…P distance of 2.950(7) Å.

Electrochemical measurements revealed reversible Fc-related redox processes, except for **13**. The latter possesses its HOMO distributed over the  $Fe_3(CO)_{10}P$  cluster core rather than the ferrocenyl entity as shown by DFT calculations

# **Experimental Section**

**General**. All reactions were performed under an atmosphere of argon using standard Schlenk techniques. Reaction flasks (Schlenk tubes) were heated at reduced pressure with a heat gun and flushed with argon. This procedure was repeated thrice. If necessary, solvents were deoxygenated by standard procedures. For column chromatography silica with a particle size of 40–60  $\mu$ m (230–400 mesh (ASTM)) was used. The assignment of *a*-(axial) and e-(equatorial) for substituents at butterfly-type fragments refers to the positioning of the Fc group, even if Cl substituents are present, possessing a higher priority contrary to H. This simplifies the discussion regarding the configuration of the ferrocenyl group at each phosphorous atom.

**Reagents.** Tetrahydrofuran was purified by distillation from sodium/benzophenone ketyl. Dichloromethane, hexane and toluene were dried and purified with an MBraun SPS-800 purification system and stored over molecular sieve (4 Å). Compounds  $Fe_2(CO)_9$  (4),<sup>[55]</sup>  $FcP(O)(OEt)_2$  (1),<sup>[56]</sup>  $FcPH_2$  (3),<sup>[15]</sup>  $FcPCI_2$  (5),<sup>[15]</sup> and  $[N(^nBu)_4][B(C_6F_5)_4]^{[48,57]}$  were synthesized according to literature procedures reported elsewhere. Ferrocene, phosgene (1.9 M in toluene), Li[AlH\_4] (600 mg pallets), BuLi (<sup>*n*</sup>: 2.5 M in hexane; <sup>*t*</sup>: 1.9 M in hexane), CIP(O)(OEt)<sub>2</sub>, and Fe(CO)<sub>5</sub>, were purchased from commercial suppliers and were used without further purification.

**Instruments.** *FT-IR* spectra were recorded as KBr pallets in transition mode. *NMR* spectra were recorded with a Bruker Avance III 500 spectrometer (500.3 MHz for <sup>1</sup>H, 125.8 MHz for <sup>13</sup>C and 202.5 MHz for <sup>31</sup>P) and are reported with chemical shifts in  $\delta$  (ppm) units downfield from tetramethylsilane with the solvent as the reference signal (chloroform- $d_1$ : <sup>1</sup>H at 7.26 ppm and <sup>13</sup>C{<sup>1</sup>H} at 77.16 ppm), or by the <sup>2</sup>H solvent lock signal.<sup>[58]</sup> Two decimal places for <sup>13</sup>C{<sup>1</sup>H} values are given to clarify the assignment of signals, which are in close proximity to each other. The *melting* or decomposition points were determined by using a Gallenkamp MFB 595 010 M melting point apparatus. Elemental analyses were performed with a Thermo FlashAE 1112 instrument.

**Electrochemistry**. Electrochemical measurements of the respective compounds (1.0 mmol·L<sup>-1</sup>) using 0.1 mol·L<sup>-1</sup> [N<sup>n</sup>Bu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as the supporting electrolyte in anhydrous, oxygen-free dichloromethane were performed in an argon purged cell at 25 °C with a Radiometer Voltalab PGZ 100 electrochemical workstation inter-



faced with a personal computer.<sup>[57]</sup> For the voltammetric measurements a three electrode cell containing a Pt auxiliary electrode, a glassy carbon working electrode (surface area 0.031 cm<sup>2</sup>) and an  $Ag/Ag^+$  (0.01 mmolL<sup>-1</sup> [AgNO<sub>2</sub>]) reference electrode fixed on a Luggin capillary was used. The working electrode was pretreated by polishing on a Buehler microcloth first with 1  $\mu$ m and then with a  $1/_4$  µm diamond paste. The reference electrode was constructed from a silver wire inserted into a 0.01 mmol L<sup>-1</sup> solution of [AgNO<sub>3</sub>] and 0.1 mol L<sup>-1</sup> of an  $[N^n Bu_4][B(C_6 F_5)_4]$  acetonitrile solution in a Luggin capillary with a CoralPor tip. This Luggin capillary was inserted in a second Luggin capillary containing a 0.1 mol  $L^{-1}$  $[N^n Bu_4][B(C_6 F_5)_4]$  dichloromethane solution and a CoralPor tip. Experiments under the same conditions showed that all reduction and oxidation potentials were reproducible within  $\pm 5$  mV. Experimental potentials were referenced against an Ag/Ag<sup>+</sup> reference electrode, but the presented results are referenced against ferrocene as an internal standard as required by IUPAC.<sup>[59]</sup> To achieve this, each experiment was repeated in the presence of 1 mmol L<sup>-1</sup> of decamethylferrocene (Fc\*). Data were processed on a Microsoft Excel worksheet to set the formal reduction potentials of the FcH/FcH<sup>+</sup> couple to 0.0 V.<sup>[60]</sup> Under our conditions the Fc\*/Fc\*<sup>+</sup> couple was at -614 mV vs FcH/FcH<sup>+</sup>,  $\Delta E_p = 60 \text{ mV}$ , while the FcH/ FcH<sup>+</sup> couple itself was at 220 mV vs Ag/Ag<sup>+</sup>,  $\Delta E_p = 61$  mV.

**Spectroelectrochemistry**. Spectroelectrochemical IR measurements of 2.0 mmol·L<sup>-1</sup> solutions of **14** and **17** in anhydrous dichloromethane containing 0.1 mol·L<sup>-1</sup> of  $[N^{n}Bu_{4}][B(C_{6}F_{5})_{4}]$  as the supporting electrolyte were performed in an OTTLE (=Optically Transparent Thin-Layer Electrochemical) cell with CaF<sub>2</sub> windows at a Varian Cary 5000 spectrophotometer at 25 °C.

Single crystal X-ray diffraction analysis. Data were collected with an Oxford Gemini S diffractometer (*a,a*-12 *a*, and 14–20) and a Venture D8 diffractometer (*a*-11, 13) with Cu K<sub>a</sub> radiation ( $\lambda$  = 1.54184 Å; 13) and Mo K<sub>a</sub> radiation ( $\lambda$  = 0.71073 Å, *a*-11, *a,a*-12 *a*, 14–20) at 125 K (*a,a*-12 *a*, 14–20) and ambient conditions (*a*-11, 13). Measurements with Cu K<sub>a</sub> radiation at the D8 Venture device were performed with a fine-focus source. The molecular structures were solved by direct methods using SHELXS-13<sup>[61]</sup> and refined by fullmatrix least-squares procedures on *F*<sup>2</sup> using SHELXL-13.<sup>[62,63]</sup> All nonhydrogen atoms were refined anisotropically and a riding model was employed in the treatment of the hydrogen atom positions, except otherwise noted. Graphics of the molecular structures have been created by using ORTEP.<sup>[64]</sup>

Deposition Numbers 1999233 (a-11), 1999234 (13), 1935472 (14), 1999235 (a,a-12a), 1999236 (15), 1999237 (16), 1999238 (17), 1999239 (18), 1999240 (19), and 1999241 (20) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

**Computational methods**. DFT calculations were performed with the Orca 4.2.1 suite using ZORA scalar-relativistic correction.<sup>[65]</sup>

## Reaction of FcPCl<sub>2</sub> (5) with Fe<sub>2</sub>(CO)<sub>9</sub> (10)

Phosphine **5** (500 mg, 1.75 mmol) and **10**, (3.82 g, 10.5 mmol) were reacted in 50 mL of toluene at  $45-50^{\circ}$ C for 30 min. All volatiles were removed in vacuo. The residue was taken up in 30 mL of dichloromethane, mixed with silica and evaporated to dryness. This mixture was put on a column (silica,  $20 \times 3.5$  cm) and hexane was used to remove Fe<sub>3</sub>(CO)<sub>12</sub> as the first, intense green fraction. Changing the eluent to a 4:1 hexane/toluene mixture (*v*/*v*) eluted **11**, **13** and **14** as red bands. After removal of all volatiles all compounds were obtained as purple-red solids.

When 750 mg (2.61 mmol) of **5** and 950 mg (2.61 mmol) of **10** were reacted in 30 mL of toluene under equal conditions a mixture of compounds **12a–c** could be eluted using a 4:1 hexane/ toluene mixture (v/v) from a silica column. Subsequent purification (silica, 20×3.5 cm) with the same solvent mixture allowed for the separation of a 3:1 mixture of a,a-12a/e,e-12a (6.3 mg, 0.008 mmol, 0.6% based on **5**), and compound a,a-12b. After removal of all volatiles, all compounds were obtained as orange-yellow solids. Single crystals were grown from slow evaporation of dichloromethane mixtures of the respective compound at ambient conditions.

**Fe<sub>2</sub>(CO)<sub>6</sub>(μ<sub>2</sub>-CI)(μ<sub>2</sub>-PCIFc)** (11): The compound was obtained as a ~ 3.3:1 mixture of the *a*- (major) and the *e*-isomer (minor) of 11. (All H atoms are summed up to a total of  $3.3 \cdot 9 + 9$  H = 38.7 H. HSQC and HMBC data support the assignment.) Yield: 44 mg (0.04 mmol, 4% based on 5). Red solid. IR data (KBr, v<sup>-</sup>): 2078 (vs), 2044 (s), 2020 (s), 2014 (s), 1986 (vs), 1969 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>16</sub>H<sub>9</sub>Cl<sub>2</sub>Fe<sub>3</sub>O<sub>6</sub>P (566.65 g/mol): C, 33.91; H, 1.60. Found: C, 35.63; H, 1.91 (toluene impurities). Mp: 120 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 4.37 (s, 21.5 H, *a*-*e*-C<sub>5</sub>H<sub>5</sub>), 4.493–4.494 (m, 13.2H, *a*-C<sub>5</sub>H<sub>4</sub>), 4.62–4.63 (m, 2H, *e*-C<sub>5</sub>H<sub>4</sub>), 4.62–4.63 (m, 2H, *e*-C<sub>5</sub>H<sub>4</sub>) ppm. <sup>13</sup>C[<sup>1</sup>H} NMR (CDCl<sub>3</sub>,  $\delta$ ): 70.77 (s, *a*-C<sub>5</sub>H<sub>5</sub>), 70.87 (s, *e*-C<sub>5</sub>H<sub>5</sub>), 71.9 (d, *J*<sub>CP</sub> = 9.1 Hz, *a*-C<sub>5</sub>H<sub>4</sub>), 72.5 (d, *J*<sub>CP</sub> = 8.9 Hz, *e*-C<sub>5</sub>H<sub>4</sub>), 73.44 (d, *J*<sub>CP</sub> = 14.18 Hz, *e*-C<sub>5</sub>H<sub>4</sub>), 73.48 (d, *J*<sub>CP</sub> = 13.29 Hz, *a*-C<sub>5</sub>H<sub>4</sub>), 78.7 (d, <sup>1</sup>*J*<sub>CP</sub> = 8.5 Hz, *a*-C–P), 207.7 (br s, *e*-CO), 207.9 (br s, *a*-CO) ppm. (The *e*-C–P signal could not be resolved.) <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>,  $\delta$ ): 225.5 (*a*-isomer), 263.9 (*e*-isomer) ppm.

Crystal Data for *a*-11: C<sub>16</sub>H<sub>9</sub>Cl<sub>2</sub>Fe<sub>3</sub>O<sub>6</sub>P, *M*=566.65 g mol<sup>-1</sup>, intense red plate, 0.2·0.2·0.1, monoclinic, *P*2<sub>1</sub>/*c*,  $\lambda$ =1.54178 Å, *a*= 12.8422(6) Å, *b*=20.1801(9) Å, *c*=7.7843(4) Å,  $\beta$ =93.608(3), *V*= 2013.36(17) Å<sup>3</sup>, *Z*=4,  $\rho_{calcd}$ =1.869 Mg m<sup>-3</sup>,  $\mu$ =20.588 mm<sup>-1</sup>, *F*<sub>000</sub>= 1120, *T*=298 K,  $\theta$  range 3.448 – 65.480°, 41144 reflections collected, 3429 independent reflections (*R*<sub>int</sub>=0.0777), 253 parameters, 0 restraints, *GooF*=1.030, *R*<sub>1</sub>=0.0373, *wR*<sub>2</sub>=0.0957 (*I* > 2 $\sigma$ (*I*)).

*a*,*a*-Fe<sub>2</sub>(CO)<sub>6</sub>( $\mu_2$ -PCIFc)<sub>2</sub> (*a*,*a*-12a): Present with 75% in a mixture with *e*,*e*-12a. Orange solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 4.03–4.01 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 4.22–4.20 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 4.22 (s, 10H, C<sub>5</sub>H<sub>5</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>,  $\delta$ ): 70.8 (s, C<sub>5</sub>H<sub>5</sub>), 71.0 (t, *J*<sub>CP</sub>=5.3 Hz, C<sub>5</sub>H<sub>4</sub>), 75.6 (t, *J*<sub>CP</sub>=8.0 Hz, C<sub>5</sub>H<sub>4</sub>), 86.4 (dd, <sup>1</sup>*J*<sub>CP</sub>=9.5 Hz, <sup>3</sup>*J*<sub>CP</sub>=7.8 Hz, C–P), 210.8 (t, <sup>2</sup>*J*<sub>CP</sub>=4.1 Hz, CO) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>,  $\delta$ ): 247.3 (s) ppm. <sup>31</sup>P

Crystal Data for *a*,*a*-**12 a**:  $C_{26}H_{18}Cl_2Fe_4O_6P_2$ ,  $M=782.64 \text{ gmol}^{-1}$ , orange block, 0.2·0.2·0.05, monoclinic, C2/c,  $\lambda = 0.71073 \text{ Å}$ , a = 20.0095(11) Å, b = 9.4911(4) Å, c = 14.7351(7) Å,  $\beta = 93.179(5)^{\circ}$ ,  $V = 2794.1(2) \text{ Å}^3$ , Z=4,  $\rho_{calcd} = 1.861 \text{ Mg m}^{-3}$ ,  $\mu = 2.382 \text{ mm}^{-1}$ ,  $F_{000} = 1560$ , T = 125.5(6) K,  $\theta$  range  $3.347-25.000^{\circ}$ , 7823 reflections collected, 2459 independent reflections ( $R_{int} = 0.0463$ ), 181 parameters, 0 restraints, GooF = 1.019, R1 = 0.0321, wR2 = 0.0665 ( $I > 2\sigma(I)$ ).

*e*,*e*-Fe<sub>2</sub>(CO)<sub>6</sub>(μ<sub>2</sub>-PCIFc)<sub>2</sub> (*e*,*e*-12a): Present with 25% in a mixture with *a*,*a*-12a. Orange solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 4.36 (s, 10H, C<sub>5</sub>H<sub>5</sub>), 4.61–4.50 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 4.79–4.81 (m, 4H, C<sub>5</sub>H<sub>4</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>,  $\delta$ ): 71.0 (s, C<sub>5</sub>H<sub>5</sub>), 72.1 (t, *J*<sub>CP</sub>=4.7 Hz, C<sub>5</sub>H<sub>4</sub>), 73.6 (t, *J*<sub>CP</sub>=7.3 Hz, C<sub>5</sub>H<sub>4</sub>), 210.0 (t, <sup>2</sup>*J*<sub>CP</sub>=4.3 Hz, CO) ppm (the signal of the *ipso* carbon could not be resolved). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>,  $\delta$ ): 254.4 (s) ppm.

*a*,*e*-Fe<sub>2</sub>(CO)<sub>6</sub>( $\mu_2$ -PCIFc)<sub>2</sub> (*a*,*e*-12a): Solely identified from initial mixture of isomers of 12a-c (See Figure S6). <sup>1</sup>H NMR (CDCI<sub>3</sub>,  $\delta$ ): could not be assigned from the mixture. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCI<sub>3</sub>,  $\delta$ ): 70.88 (s, C<sub>5</sub>H<sub>5</sub>), 70.89 (s, C<sub>5</sub>H<sub>5</sub>), 71.9 (d,  $J_{C,P}$ =9.6 Hz, C<sub>5</sub>H<sub>4</sub>), 75.9 (d,  $J_{C,P}$ =15.7 Hz, C<sub>5</sub>H<sub>4</sub>), 210.3 (t, <sup>2</sup> $J_{C,P}$ =4.2 Hz, CO) ppm. Further signals could not unambiguously be assigned. <sup>31</sup>P{<sup>1</sup>H}<sup>31</sup>P NMR (CDCI<sub>3</sub>,  $\delta$ ): 245.3 (d, <sup>2</sup> $J_{C,P}$ =109.2, P<sup>a</sup>), 255.0 (d, <sup>2</sup> $J_{C,P}$ =109.1 Hz, P<sup>e</sup>) ppm.



*a*,*a*-Fe<sub>2</sub>(CO)<sub>6</sub>(μ-PCIFc)(μ-PHFc) (*a*,*a*-12b): Yield: 5 mg (0.007 mmol, 0.3% based on 5). Orange solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 3.98 (dd, <sup>1</sup>*J*<sub>H,P</sub>= 386.6 Hz, <sup>3</sup>*J*<sub>P,P</sub> = 8.7 Hz, 1H, PH)\*, 4.25 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.36 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.46–4.45 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 4.49–4.47 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 4.54–4.52 (m, 4H, C<sub>5</sub>H<sub>4</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, δ): 70.4 (<sup>1</sup>*J*<sub>C,P</sub>=2.1 Hz, C–P<sup>H</sup>), 70.4 (s, C<sub>5</sub>H<sub>5</sub>), 70.9 (s, C<sub>5</sub>H<sub>5</sub>), 71.5 (d, *J*<sub>C,P</sub>=10.0 Hz, C<sub>5</sub>H<sub>4</sub>), 71.9 (d, *J*<sub>C,P</sub>=8.4 Hz, C<sub>5</sub>H<sub>4</sub>), 73.5 (dd, *J*<sub>C,P</sub>=11.8, 2.6 Hz, C<sub>5</sub>H<sub>4</sub>), 73.9 (d, *J*<sub>C,P</sub>=11.8 Hz, C<sub>5</sub>H<sub>4</sub>), 82.5 (<sup>1</sup>*J*<sub>C,P</sub>=21.7 Hz, C–P<sup>Cl</sup>), 211.6 (t, <sup>2</sup>*J*<sub>C,P</sub>=4.7 Hz, CO) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, δ): 72.3 (dd, <sup>1</sup>*J*<sub>P,H</sub>=387.2 Hz, <sup>2</sup>*J*<sub>P,P</sub>=113.8 Hz, P<sup>H</sup>), 248.5 (dd, <sup>2</sup>*J*<sub>P,P</sub>=113.8 Hz, <sup>3</sup>*J*<sub>P,H</sub>=8.4 Hz, P<sup>Cl</sup>) ppm. \*The signal partially overlaps with one of the C<sub>6</sub>H<sub>6</sub> moieties.

*e,a*-Fe<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -PCIFc)( $\mu$ -PHFc) (*e,a*-12 b): The compound could solely be identified from the initial mixture of isomers of 12a-c. <sup>31</sup>P {<sup>1</sup>H} NMR (CDCI<sub>3</sub>,  $\delta$ ): 75.7 (d, <sup>2</sup>J<sub>P,P</sub> = 148.3 Hz, P<sup>H</sup>), 268.9 (d, <sup>2</sup>J<sub>P,P</sub> = 148.4 Hz, P<sup>CI</sup>) ppm. <sup>31</sup>P NMR (CDCI<sub>3</sub>,  $\delta$ ): 75.7 (dd, <sup>2</sup>J<sub>P,P</sub> = 148.3, <sup>1</sup>J<sub>P,H</sub> = 404.3 Hz, P<sup>H</sup>), 268.9 (dd, <sup>2</sup>J<sub>P,P</sub> = 148.3, <sup>3</sup>J<sub>P,H</sub> = 23.0 Hz, P<sup>CI</sup>) ppm.

*e*,*e*-Fe<sub>2</sub>(CO)<sub>6</sub>( $\mu_2$ -PHFc)<sub>2</sub> (*e*,*e*-12 c): The compound could solely be identified from the initial mixture of isomers of 12a–c. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>,  $\delta$ ): 83.4 (s) ppm. <sup>31</sup>P NMR (CDCl<sub>3</sub>,  $\delta$ ): 83.4 (dd, <sup>1</sup>J<sub>P,H</sub>=319.3, <sup>3</sup>J<sub>P,H</sub>=85.3 Hz) ppm.

**Fe<sub>3</sub>(CO)<sub>10</sub>(μ<sub>3</sub>-PFc) (13)**: Yield: 84 mg (0.16 mmol, 8% based on FcPCl<sub>2</sub>). Red solid. IR data (KBr, v): 2080 (m), 2006 (vs), 1987 (w), 1974 (w), 1956 (s), 1809 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>20</sub>H<sub>9</sub>Fe<sub>4</sub>O<sub>10</sub>P·3/ 2 C<sub>6</sub>H<sub>14</sub> (663.63·3/2 86.18 g/mol): C, 45.09; H, 3.07. Found: C, 44.62; H, 3.57. Mp: 132°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 4.45 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.90–4.92 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 5.03–5.05 (m, 2H, C<sub>5</sub>H<sub>4</sub>) ppm. <sup>13</sup>Cl<sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 71.3 (s, C<sub>5</sub>H<sub>5</sub>), 73.6 (d, J<sub>CP</sub>=9.2 Hz, C<sub>5</sub>H<sub>4</sub>), 75.4 (d, J<sub>CP</sub>=12.5 Hz, C<sub>5</sub>H<sub>4</sub>), 212.6 (s, CO) ppm. (The signal of the C–P carbon atom was not resolved.) <sup>31</sup>Pl<sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 452.4 ppm.

Crystal Data for **13**:  $C_{20}H_9Fe_4O_{10}P$ ,  $M = 663.64 \text{ g mol}^{-1}$ , intense violetred plate,  $0.2 \cdot 0.1 \cdot 0.05$ , monoclinic,  $P2_1/n$ ,  $\lambda = 1.54184$  Å, a = 11.342(2) Å, b = 9.035(5) Å, c = 23.488(5) Å,  $\beta = 102.535(5)$ , V = 2349.6(17) Å<sup>3</sup>, Z = 4,  $\rho_{calcd} = 1.876$  Mg m<sup>-3</sup>,  $\mu = 20.553$  mm<sup>-1</sup>,  $F_{000} = 1312$ , T = 299 K,  $\theta$  range  $3.856 - 65.497^{\circ}$ , 18017 reflections collected, 3987 independent reflections ( $R_{int} = 0.0510$ ), 316 parameters, 0 restraints, GooF = 1.113,  $R_1 = 0.0414$ ,  $wR_2 = 0.0811$  ( $I > 2\sigma(I)$ ).

**Fe<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-PFc)<sub>2</sub> (14)**: Yield: 220 mg (0.32 mmol, 16% based on FcPCl<sub>2</sub>). IR data (KBr, *v*<sup>\*</sup>): 2065 (w), 2035 (vs), 2013 (s), 1994 (m) cm<sup>-1</sup>. Red solid. Anal. Calcd for C<sub>29</sub>H<sub>18</sub>Fe<sub>5</sub>O<sub>9</sub>P<sub>2</sub> (851.62 g/mol): C, 40.90; H, 2.13. Found: C, 40.75; H, 2.52. Mp: 132 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 4.39 (s, 10H, C<sub>5</sub>H<sub>4</sub>), 4.64–4.66 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 4.69–4.71 (m, 4H, C<sub>5</sub>H<sub>4</sub>) ppm. <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>,  $\delta$ ): 70.8 (s, C<sub>5</sub>H<sub>5</sub>), 72.8 (br, s, C<sub>5</sub>H<sub>4</sub>), 73.9 (br, C<sub>5</sub>H<sub>4</sub>), 213.3 (s, CO) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>,  $\delta$ ): 316.2 ppm. Spectroscopic data and a crystal structure of **14** have recently been published by our group<sup>16</sup> and can be obtained via CCDC number: 1935472.

## Reaction of $[Fe(\eta^{5}-C_{5}H_{4}PCI_{2})_{2}]$ (6) with $Fe_{2}(CO)_{9}$ (10)

Compound **6** (510 mg, 1.44 mmol) and **10**, (2.77 g, 7.61 mmol) were reacted in 150 mL of toluene at 45–50 °C for 1 h. All volatiles were removed in vacuo and the residue was purified using column chromatography (silica). Using hexane removed  $Fe_3(CO)_{12}$  as the first, intense green fraction, followed by **15** (17 mg) and **16** (2 mg) as pale green bands. Changing the eluent to a 4:1 hexane/toluene mixture (*v*/*v*) gave **17** (39 mg) and **18** (14 mg) as pale yellow fractions. After removal of all volatiles all compounds were obtained as solids.

When 730 mg (2.07 mmol) of **6** and 10.53 g (28.94 mmol) of **10** were reacted in 250 mL of toluene solely **17** (100 mg, 0.17 mmol, 8%) and **18** (6.4 mg, 0.006 mmol, < 1%) were obtained.

**Fe<sub>2</sub>(CO)<sub>6</sub>(μ<sub>2</sub>-[Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>PH)<sub>2</sub>]) (15)**: Yield: 17 mg (0.032 mmol, 2% based on **6**). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 4.28 (t, J<sub>H,H</sub> = 1.9 Hz, 4H, C<sub>5</sub>H<sub>4</sub>), 4.56 (pt, J<sub>H,H</sub> = 1.7 Hz, 4H, C<sub>5</sub>H<sub>4</sub>), 5.48 (dd, <sup>1</sup>J<sub>H,P</sub> = 294.5,<sup>[66]</sup> <sup>3</sup>J<sub>H,P</sub> = 76.3 Hz, 1H, PH) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>,  $\delta$ ): 55.5 (s) ppm. No signals could be detected in the <sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P NMR, due to the small amount of compound.

Crystal Data for **15**: C<sub>16</sub>H<sub>10</sub>Fe<sub>3</sub>O<sub>6</sub>P<sub>2</sub>,  $M = 527.73 \text{ gmol}^{-1}$ , yellow block, 0.2·0.2·0.1, triclinic, P-1,  $\lambda = 0.71073 \text{ Å}$ , a = 7.5447(7) Å, b = 11.2403(9) Å, c = 11.9775(10) Å,  $a = 64.246(8)^{\circ}$ ,  $\beta = 80.782(8)^{\circ}$ ,  $\gamma = 83.940(7)^{\circ}$ ,  $V = 902.30(15) \text{ Å}^3$ , Z = 2,  $\rho_{calcd} = 1.942 \text{ Mg m}^{-3}$ ,  $\mu = 2.588 \text{ mm}^{-1}$ ,  $F_{000} = 524$ , T = 125.00(10) K,  $\theta$  range  $3.129-25.000^{\circ}$ , 11140 reflections collected, 3142 independent reflections ( $R_{int} = 0.0331$ ), 252 parameters, 0 restraints, GooF = 1.034, R1 = 0.0293, wR2 = 0.0724 ( $I > 2\sigma(I)$ ).

**Fe<sub>2</sub>(CO)<sub>6</sub>(μ<sub>2</sub>-[Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>PCI)(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>PH)])** (16): Yield: 2 mg (0.004 mmol, < 1% based on 6). <sup>1</sup>H NMR (CDCI<sub>3</sub>, δ): 4.31 (pt\*, *J*<sub>H,H</sub> = 2.0 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 4.38 (pt\*, *J*<sub>H,H</sub> = 2.0 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 4.61 (dd\*, *J* = 2.2, 2.0 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 4.79 (dd\*, *J* = 2.2, 2.0 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 5.67 (dd, <sup>1</sup>*J*<sub>H,P</sub> = 365.1 Hz, <sup>3</sup>*J*<sub>H,P</sub> = 14.1 Hz, 1H, PH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCI<sub>3</sub>, δ): no signals could be detected, due to the small amount of compound. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCI<sub>3</sub>, δ): 52.9 (d, <sup>2</sup>*J*<sub>P,P</sub> = 142.9 Hz, PH), 227.0 (d, <sup>2</sup>*J*<sub>P,P</sub> = 143.3 Hz, P–CI) ppm. \*Coupling constants were obtained from fitted spectra (see ESI)

Crystal Data for **16**: C<sub>16</sub>H<sub>9</sub>CIFe<sub>3</sub>O<sub>6</sub>P<sub>2</sub>,  $M = 562.17 \text{ gmol}^{-1}$ , pale orange plate, 0.2·0.2·0.02, triclinic, P = 1,  $\lambda = 0.71073 \text{ Å}$ , a = 7.6655(8) Å, b = 9.9831(13) Å, c = 13.5566(15) Å,  $a = 70.130(11)^{\circ}$ ,  $\beta = 84.563(9)^{\circ}$ ,  $\gamma = 74.880(10)^{\circ}$ ,  $V = 941.9(2) \text{ Å}^3$ , Z = 2,  $\rho_{calcd} = 1.982 \text{ Mg m}^{-3}$ ,  $\mu = 2.623 \text{ mm}^{-1}$ ,  $F_{000} = 556$ , T = 126(2) K,  $\theta$  range 3.094–25.000°, 7819 reflections collected, 3297 independent reflections ( $R_{int} = 0.0570$ ), 257 parameters, 357 restraints, GooF = 1.058, R1 = 0.0676, wR2 = 0.1598 ( $l > 2\sigma(l)$ ).

**Fe<sub>2</sub>(CO)<sub>6</sub>(μ<sub>2</sub>-[Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>PCI)<sub>2</sub>]) (17)**: Yield: 39 mg (0.065 mmol, 5% based on **6**). IR data (KBr, *v* <sup>7</sup>): 2068 (s), 2036 (s), 2031 (s), 2007 (s), 1997 (s), 1979 (s), 1966 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, *δ*): 4.43 (dd,  $J_{H,H}$ = 1.9 Hz, 4H, C<sub>5</sub>H<sub>4</sub>), 4.76 (dt,  $J_{H,H}$ = 3.31, 1.53 Hz, 4H, C<sub>5</sub>H<sub>4</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, *δ*): 73.1 (t,  $J_{C,P}$ = 4.3 Hz, C<sub>5</sub>H<sub>4</sub>), 76.2 (t,  $J_{C,P}$ = 5 Hz, C<sub>5</sub>H<sub>4</sub>), 91.6 (dd, <sup>1</sup> $J_{C,P}$ = 18.7,  $J_{C,P}$ = 16.0 Hz, C–P), 210.7 (b, CO) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, *δ*): 216.0 (s) ppm.

Crystal Data for **17**:  $C_{16}H_8CI_2Fe_3O_6P_2$ ,  $M=596.61 \text{ gmol}^{-1}$ , orange block, 0.2·0.2·0.1, triclinic, P-1,  $\lambda = 0.71073$  Å, a = 10.0385(4) Å, b = 13.1875(4) Å, c = 15.4752(4) Å,  $a = 93.731(2)^\circ$ ,  $\beta = 105.137(3)^\circ$ ,  $\gamma = 97.128(3)^\circ$ , V = 1952.10(11) Å<sup>3</sup>, Z=4,  $\rho_{calcd} = 2.030 \text{ Mgm}^{-3}$ ,  $\mu = 2.670 \text{ mm}^{-1}$ ,  $F_{000} = 1176$ , T = 125.9(8) K,  $\theta$  range 2.977–24.999°, 25982 reflections collected, 6833 independent reflections ( $R_{int} = 0.0389$ ), 524 parameters, 0 restraints, GooF = 1.052, R1 = 0.0403, wR2 = 0.1024 ( $I > 2\sigma(I)$ ).

**Bis{Fe<sub>2</sub>(CO)<sub>6</sub>(μ<sub>4</sub>-2,3-diphospha[2]ferrocenophanediyl)**} (18): Yield: 14 mg (0.013 mmol, 2% based on 6). IR data (KBr, v<sup>-</sup>): 2050 (m), 2031 (s), 2014 (w), 1989 (s), 1980 (vw), 1958 (s), 1944 (vw), 1916 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 4.24 (pt,  $J_{H,H}$  = 1.7 Hz, 4H,  $C_5H_4$ ), 5.19 (pt,  $J_{H,H}$  = 1.8 Hz, 4H,  $C_5H_4$ ) ppm. <sup>13</sup>C[<sup>1</sup>H} NMR (CDCl<sub>3</sub>, δ): 72.3\* ppm. <sup>31</sup>P[<sup>1</sup>H} NMR (CDCl<sub>3</sub>, δ): 139.1 (s) ppm. (\*Solely observed as a singlet; further signals were not resolved.)

Crystal Data for **18**:  $C_{32}H_{16}Fe_6O_{12}P_4$ ,  $M = 1051.43 \text{ gmol}^{-1}$ , red block, 0.2·0.2·0.1, tetragonal, *P*-4*n*2,  $\lambda = 0.71073 \text{ Å}$ , a = 10.1230(3) Å, c = 17.2619(8) Å,  $V = 1051.43(2) \text{ Å}^3$ , Z = 2,  $\rho_{calcd} = 1.974 \text{ Mgm}^{-3}$ ,  $\mu = 2.640 \text{ mm}^{-1}$ ,  $F_{000} = 1040$ , T = 125.2(2) K,  $\theta$  range  $3.081-24.993^\circ$ , 12408 reflections collected, 1537 independent reflections ( $R_{int} = 0.0372$ ), 123 parameters, 0 restraints, GooF = 1.099, R1 = 0.0181, wR2 = 0.0407 ( $I > 2\sigma(I)$ ), absolute structure parameter<sup>38</sup> 0.021(10).



# Reaction of $[Fe(\eta^{5}-C_{5}H_{3}-1,2-(PCI_{2})_{2})(\eta^{5}-C_{5}H_{5})]$ (9) with $Fe_{2}(CO)_{9}$ (10)

Compound **9** (740 mg, 2.07 mmol) and **10** (10.57 g, 29.06 mmol) were reacted in 150 mL of toluene at 45–50 °C for 1 h. All volatiles were removed in vacuo and the residue was purified using column chromatography (silica). Using hexane removed  $Fe_3(CO)_{12}$  as the first, intense green fraction. The solvent was changed to a 4:1 hexane/toluene mixture (*v*/*v*), which eluted **20** and **19** as short yellow fractions. After removal of all volatiles both compounds were obtained as yellow solids.

 $(R_p, S_p)$ -Bis(Fe<sub>2</sub>(CO)<sub>6</sub>{μ<sub>4</sub>-[Fe(C<sub>5</sub>H<sub>5</sub>)(1-PCl-2-P-C<sub>5</sub>H<sub>3</sub>)]}-1κ<sup>2</sup>P<sup>1</sup>, P<sup>2'</sup>-2κ<sup>2</sup>P<sup>1</sup>, P<sup>2'</sup>) (19): Yield: 6 mg (0.006 mmol, 0.3 % based on 9). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): signals could not unambiguously be assigned. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>,  $\delta$ ): 73.2 (C<sub>5</sub>H<sub>5</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>,  $\delta$ ): 118.7 (dd,  $J_{P,P}$ =77.1, 65.1 Hz, P<sup>-P</sup>), 238.2 (dd,  $J_{P,P}$ =78.7, 64.6 Hz, P<sup>C</sup>) ppm.

Crystal Data for **19**:  $C_{32}H_{16}Cl_2Fe_6O_{12}P_4$ ,  $M = 1122.33 \text{ gmol}^{-1}$ , red block, 0.05 · 0.05 · 0.05, triclinic, P-1,  $\lambda = 0.71073$  Å, a = 10.605(2) Å, b = 10.707(3) Å, c = 17.196(3) Å,  $\alpha = 81.279(18)^\circ$ ,  $\beta = 73.367(17)^\circ$ ,  $\gamma = 86.628(19)^\circ$ , V = 1849.0(7) Å<sup>3</sup>, Z = 2,  $\rho_{calcd} = 2.016 \text{ Mg m}^{-3}$ ,  $\mu = 2.672 \text{ mm}^{-1}$ ,  $F_{000} = 1108$ , T = 124.8(6) K,  $\theta$  range 2.931–24.999°, 15214 reflections collected, 6486 independent reflections ( $R_{int} = 0.1426$ ), 469 parameters, 675 restraints, GooF = 0.891, R1 = 0.0833, wR2 = 0.1235 ( $l > 2\sigma(l)$ ).

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Crystal Data for **20**:  $C_{32}H_{16}Cl_2Fe_6O_{12}P_4$ ,  $M = 1122.33 \text{ gmol}^{-1}$ , red block, 0.2·0.2·0.1, monoclinic, C2/c,  $\lambda = 0.71073 \text{ Å}$ , a = 19.7315(10) Å, b = 16.4009(7) Å, c = 11.3186(5) Å,  $\beta = 91.195(4)^\circ$ ,  $V = 3662.1(3) \text{ Å}^3$ , Z = 4,  $\rho_{calcd} = 2.698 \text{ Mgm}^{-3}$ ,  $\mu = 2.698 \text{ mm}^{-1}$ ,  $F_{000} = 2216$ , T = 125.1(2) K,  $\theta$  range  $3.231 - 24.999^\circ$ , 7328 reflections collected, 3222 independent reflections ( $R_{int} = 0.0344$ ), 253 parameters, 0 restraints, GooF = 1.028, R1 = 0.0348, wR2 = 0.0706 ( $l > 2\sigma(l)$ ).

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278.8 (d, J<sub>P.P</sub>=21.5 Hz, P<sup>CI</sup>) ppm.

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# **Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** Ferrocene · Phosphine · Iron Carbonyl · Cluster · Electrochemistry · Phosphinidene

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# **FULL PAPERS**



The reaction of  $Fe_2(CO)_9$  with ferrocenyl(bis)dichlorophosphines is investigated. The products contain butterfly motifs, phosphinidene cluster cores in dependence of the ferrocenyl's substitution pattern. Compounds including

P-P bonds gave organometallic octabisvalene and novel  $\mu,\kappa^{8}$ -coordinating motifs. Single crystal structures, NMR, IR, EC and DFT calculations confirm their identity and properties in various charged states.

Structural Variety of Iron Carbonyl **Clusters Featuring Ferrocenyl-**

phosphines