1,2-Diphosphetene, 1,2-Diphosphete, and 1,3-Diphosphete Metal Complexes: Novel Access by Ring Contraction, Cyclodimerization, and Intramolecular Redox Reactions†

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The reaction of [Cr(CO)$_5$(THF)] and pentaphenyl-1,2,3-triphospholene affords a single stereoisomer of [(pentaphenyl-1,3-η-1,2,3-triphospholene)(Cr(CO)$_5$)$_2$] (**6**). Visible light photolysis of **6** causes a ring contraction and [(*trans*-tetraphenyl-1,2-η-1,2-diphosphetene)(Cr(CO)$_5$)$_2$] (**7a**) is formed, whose stereochemistry was elucidated by X-ray crystallography. *trans*-1,2-Dichloro-3,4-di-*tert*-butyl-1,2-diphosphetene (**2a**) and [Fe$_2$(CO)$_9$] form the σ complexes [(*trans*-1,2-dichloro-3,4-di-*tert*-butyl-1-η-1,2-diphosphetene)Fe(CO)$_4$] (**8a**) and [(*trans*-1,2-dichloro-3,4-di-*tert*-butyl-1,2-η-1,2-diphosphetene)(Fe(CO)$_4$)$_2$] (**8b**), depending on the relative concentration of the starting materials. **8a** has been proven to be an intermediate in the formation of **8b**. Heating of neat **8b** in a vacuum leads to the elimination of the chlorine substituents in an intramolecular redox reaction and [(3,4-di-*tert*-butyl-η^4-1,2-diphosphete)-Fe(CO)$_3$] (**9a**) is formed. This is the first specific reaction, leading to a 1,2-diphosphete complex. **9a** and its 1,3-isomer **10a** react with [Cr(CO)$_5$(THF)] to form the mono- and diaddition products [1-η-{(3,4-di-*tert*-butyl-η^4-1,2-diphosphete)Fe(CO)$_3$}Cr(CO)$_5$] (**9b**), [1,2-η-{(3,4-di-*tert*-butyl-η^4-1,2-diphosphete)Fe(CO)$_3$}(Cr(CO)$_5$)$_2$] (**9c**), [1-η-{(2,4-di-*tert*-butyl-η^4-1,3-diphosphete)Fe(CO)$_3$}Cr(CO)$_5$] (**10b**), and [1,3-η-{(2,4-di-*tert*-butyl-η^4-1,3-diphosphete)-Fe(CO)$_3$}(Cr(CO)$_5$)$_2$] (**10c**), respectively. X-ray crystallographic studies for **9c** and **10c** give some insight into the bonding situation of the compounds. σ- and π-complexing properties of the diphosphete ligands are almost independent of each other and significant back-bonding from the iron atom to the ligand π* orbitals occurs in both cases.

Introduction

The C═C double bond of the partly unsaturated cis (**1**) or trans (**2**) isomers of 1,2-diphosphetene rings $C_2R'_2P_2R_2$[1] does not interact significantly with the two lone pairs of the phosphorus atoms.[2,3] Its ligand properties reveal a comparable situation, as exclusively the P-σ lone pairs determine the behavior toward transition metals. To the best of our knowledge no complex of **1**, **2**, or topologically related unsaturated P-heterocycles has been reported as yet, in which the metal is coordinated to the π-electrons of a vinylic C═C double bond in combination with an adjacent P−M σ-bond. As the divergency of the phosphorus lone pairs and the C$_{\text{ring}}$-p$_z$ orbitals can be estimated to be in the range between 15° and 35° on the basis of the P−P−C$_{\text{substituent}}$ bond angles (Figure 1), which range from 101° to 107°,[4,5] a simultaneous interaction between both types of donor functions and a suitable transition metal seems to be possible. The divergency of the C$_{\text{ring}}$-p$_z$ orbitals of the pronounced convex surface of the π ligand of [(η^6-2,2-paracyclophane)Cr(CO)$_3$], for example, is just in that range.[6] The same topological situation of **1** and **2** is present in 1,2,3-triphospholenes (**3**).[7]

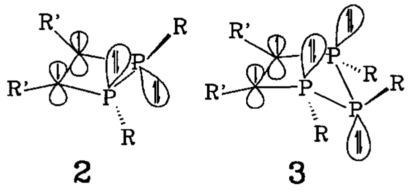

Figure 1. Relative orientations of C═C π bond and phosphorus lone pair orbitals of *trans*-1,2-diphosphetene (**2**) and 1,2,3-triphospholene (**3**) derivatives.

π-Complexes of unsaturated heterocycles exhibit frontier orbitals, which depend decisively on the heteroatom and the symmetry of the ring ligand, and these orbitals govern the reactivity of such complexes.[8] We have

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† Dedicated to Professor Otto J. Scherer on the occasion of his 65th birthday.

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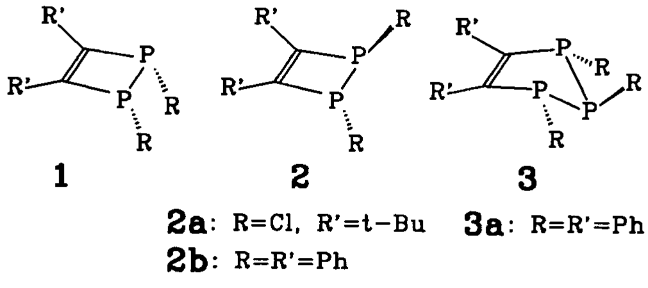
utilized this effect for a significant variation of the properties of known catalysts with carbacyclic π ligands.[9] π,σ complexes of the heterocycles **1**−**3** could be a new alternative for such an approach. Therefore we found it worthwhile to investigate the preparation of complexes in which **1**−**3** can function as four-electron- (π^2,σ^2) or even six-electron-donating (π^2,σ^2,σ^2) flat ligands.

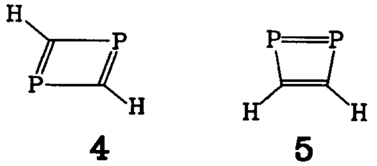
The idea is backed by the coordination chemistry of the diheterodiene species 1,2,4-triphosphole, which may act as a six-electron-donating ligand toward a $Mo(CO)_3$ fragment by including the P-lone pair into the π electron system of the ring.[11]A very bulky substituent on the saturated σ^3-P atom seems to be essential to create such a planar η^5-triphosphole ligand.

Lesser related cases are the fully unsaturated $C_2R_2P_2$ ligands 1,3-diphosphete (**4**)[10] and 1,2-diphosphete (**5**),[12] where transition metal atoms always interact with the π electrons of P and C atoms at the same time. Being antiaromatic π^4 species, **4** and **5** do not have an independent existence at ambient temperature, but require stabilization as π^4 ligands in the coordination sphere of a transition metal.[13] An additional σ^2-P−M′ interaction is possible, too, but only with a second transition metal in the plane of the ring.[10,14,15] In the case of a successful π,σ interaction between **1** or **2** and a suitable transition metal, an activation of the P-substituents toward cleavage of the bond seems to be likely, as only small structural changes within the (P-heterocycle)M substructure are necessary to convert a 1,2-diphosphetene ligand into a fully unsaturated 1,2-diphosphete by removing the substituents of the phosphorus atoms.

trans-1,2-Dichloro-3,4-di-*tert*-butyl-1,2-diphosphetene (**2a**)[16] was chosen for the experiments dealing with *trans*-1,2-diphosphetenes, as the chlorine substituents are promising leaving groups. Neglecting the P-lone pair electrons, **2a** is analogous to 3,4-dichlorocyclobutene, which was used successfully by Pettit and co-workers, when they prepared [(η^4-cyclobutadiene)$Fe(CO)_3$] as the first example of a π-cyclobutadiene transition metal complex.[17] 1,2,3,4,5-Pentaphenyl-1,2,3-triphospholene (**3a**), on the other hand, was chosen as the second starting material because of its good availability and suitable chemical properties.[4,7] According to the ^{31}P NMR spectra of purified starting material **3a**,[18] the phenyl substituents are oriented exclusively as indicated in Figure 1; thus the P-lone pairs of the adjacent P atoms 1 and 3 of the C═C double bond are directed toward the same side of the ring.

Scheme 1





Results

Reactivity of Pentaphenyl-1,2,3-triphospholene 3a. 3a was reacted with the highly reactive metal vapor product [(1,5-COD)$_2$Fe],[19] which is an excellent generator of (1,5-cyclooctadiene)Fe fragments at low temperature. These 12 valence electron (VE) fragments need donation of six additional electrons by ligands for the formation of stable 18-VE complexes.[20] A product is formed in the reaction, but it is of limited stability at room temperature. According to field desorption mass spectroscopy, it is [(COD)(pentaphenyl-1,2,3-triphospholene)Fe], and NMR spectroscopic evidence suggested coordination of P atoms P(1) and P(3) to the iron atom, since the heterocycle forms an AX_2 spin system, where the X nuclei exhibit the proposed coordination shift. Proof for or against an interaction between the iron atom and the C═C double bond is not yet possible, as to date no single crystals have been obtained.

If an excess of [$Cr(CO)_5$(THF)] is allowed to react with **3a** at room temperature in THF, the 1,3-P atoms, again, are the active centers of the heterocycle and two $Cr(CO)_5$ fragments are added to form [(1,2,3,4,5-pentaphenyl-1,3-η-1,2,3-triphospholene)($Cr(CO)_5$)$_2$] (**6**). The isolated yield is nearly quantitative, and there is no hint that the C═C double bond or P(2) is taking part in the bonding in the product. This is in line with literature reports concerning 1,2,3-triphospholene derivatives, where always only P(1) and P(3) interact with transition metal atoms.[22] According to the NMR spectra of **6**, stereochemistry and symmetry of ligand **3a** are maintained in the product. Thus the two $Cr(CO)_5$ fragments are believed to be bonded at the same side of the ring ligand (Scheme 2).

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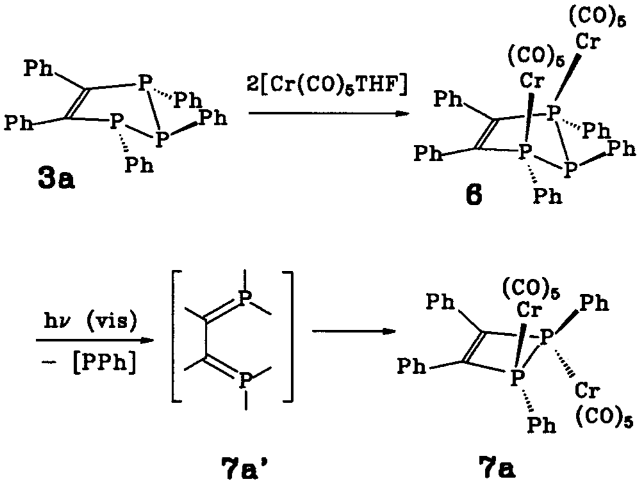
Scheme 2



An AX_2 spin system is observed in the $^{31}P\{^{1}H\}$ NMR spectrum of **6** (121.5 MHz), and the X nuclei are much more shifted than the A nucleus with respect to the signals of the free ligand, due to the direct P–Cr interaction of P(1) and P(3). The existence of a double doublet for P(2) which is split by 4.5 Hz instead of a first-order triplet can successfully be simulated. As one would expect, the stereochemistry of the ligand has not changed upon complexation.

To force the inclusion of the π electrons of the C=C double bond into the interaction between the cyclic ligand and the chromium atoms of **6**, CO elimination reactions have been tried. Heating solutions of **6** was not successful, as inseparable mixtures are formed. Visible light photolysis, however, yields a reaction mixture, whose workup allows isolation of the main product [(*trans*-1,2,3,4-tetraphenyl-1,2-η-1,2-diphosphetene)($Cr(CO)_5)_2$] (**7a**) by chromatography. To our surprise, no CO loss has taken place, but the central P(2)Ph unit was lost from the molecule and the two chromium atoms of **7a** now are in a trans position (vide infra). **7a** is therefore a complex of the ligand *trans*-1,2,3,4-tetraphenyl-1,2-diphosphetene (**2b**), and the photolysis reaction of **6** represents a new access to such complexes (Scheme 2).

Complexes of **2b** can be made directly from the ligand, but **3a** is more readily accessible.[4] [*trans*-(1,2-$C_2P_2Ph_4$)($W(CO)_5)_2$][21] (**7b**) and [*trans*-(1,2-$C_2P_2Ph_4$)($Fe(CO)_4)_2$][4,23] (**7c**) are closely related to **7a** with regard to their properties. Fe carbonyl species **7c** has already been investigated with respect to its behavior upon heating. P–P bond cleavage and loss of one molecule of PhC≡CPh were observed.[4] As found here, the C=C double bond did not interact with the metal atoms. Therefore, no more experiments in this direction have been carried out with **7a**. To prove the proposed stereochemistry, the structure of **7a** was determined by X-ray crystallography. The solid-state molecular structure of **7a** is shown in Figure 2. and some selected bond distances and angles are summarized in the figure caption.

Figure 2 clearly indicates the trans arrangement of the two $Cr(CO)_5$ fragments and the P-phenyl substituents, respectivly. The ring of **7a** is nearly planar and less twisted than in the free ligand **2b**. This is indicated by the angle between the endocyclic bonds P(1)–P(2) and C(1)–C(2), which is 7.8° for **7a**, but 19° for **2b**.[4] All bond distances and angles of **7a** are in the normal ranges, which are defined by related compounds such as **7b** and **7c**.

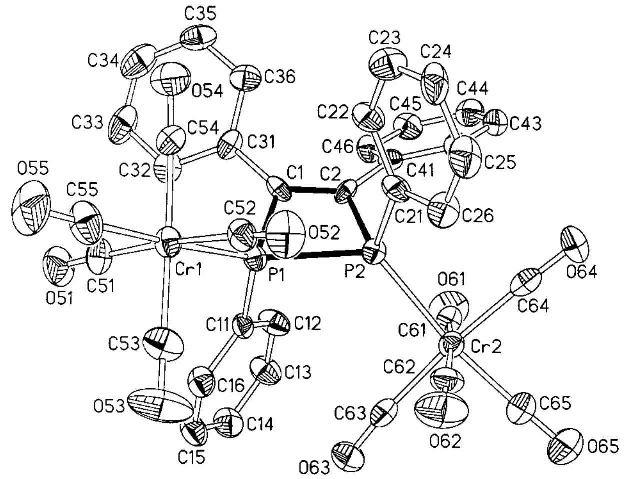


Figure 2. View of the molecular structure of [(*trans*-1,2,3,4-tetraphenyl-1,2-η-1,2-diphosphetene)($Cr(CO)_5)_2$]·C_6D_6 (**7a**) in the solid state. Selected bond distances [Å] and angles [deg]: Cr(1)–P(1), 2.348(2); Cr(2)–P(2), 2.356(2); P(1)–C(11), 1.831(6); P(2)–C(21), 1.841(6); C(1)–C(31), 1.480(8); C(2)–C(41), 1.488(8); C(1)–C(2), 1.331(8); C(1)–P(1), 1.830(6); C(2)–P(2), 1.824(6); P(1)–P(2), 2.271(2); C(2)–C(1)–P(1), 104.1(5); C(1)–P(1)–P(2), 75.1(2); P(1)–P(2)–C(2), 74.7(2); P(2)–C(2)–C(1), 105.1(5). There are no bonding interactions between C_6D_6 and **7a**. Hydrogen atoms and the C_6D_6 molecule are omitted for clarity.

Mechanistic considerations of the formation of **7a** from **6** need to explain the fact that at least one P(Ph)($Cr(CO)_5$) moiety rotates by 180° during the course of the reaction, as one of the two chromium atoms changed from one side of the ligand ring to the other. If we suppose a ring-opened structure after the P(2)Ph unit has left molecule **6**, an open chain *cis*-1,4-diphosphabutadiene, structure **7a′**, is the most probable intermediate, which allows a ring closure immediately after its formation. A related 1,2-diphosphetene → 1,4-diphosphabutadiene rearrangement has been found to date in only one example, that of ditungsten complex **7b**.[21] If the reaction sequence includes **7a′** as the decisive intermediate, the 180° rotation of one P(Ph)($Cr(CO)_5$) unit is easily understood, as both phosphorus atoms have to rotate by 90° together with their substituents, for the ring opening as well as for the ring-closure steps (Scheme 2).

Reactivity of *trans*-1,2-Dichloro-3,4-di-*tert*-butyl-1,2-diphosphetene 2a. **2a** was reacted with [$Fe_2(CO)_9$]. In contrast to **2b**, the reaction of **2a** and [$Fe_2(CO)_9$] proceeds well at room temperature.[4] Depending on the relative concentration of the reactants, one or two iron atoms became bonded to the phosphorus atoms to form [(*trans*-1,2-dichloro-3,4-di-*tert*-butyl-1-η-1,2-diphosphetene)$Fe(CO)_4$] (**8a**) and [(*trans*-1,2-dichloro-3,4-di-*tert*-butyl-1,2-η-1,2-diphosphetene)($Fe(CO)_4)_2$] (**8b**), respectively (Scheme 3). In the reaction mixture, even before workup, no traces of the corresponding cis isomers are observable.

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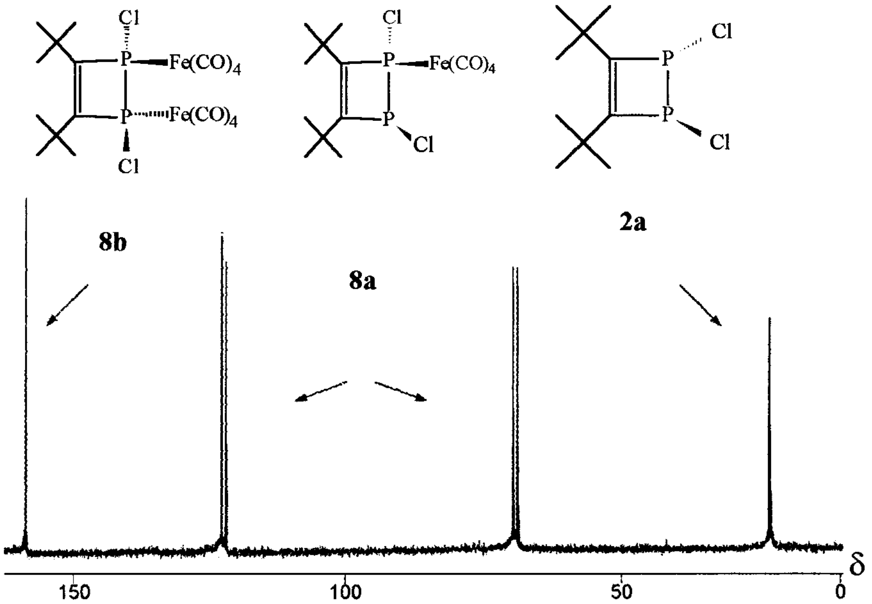
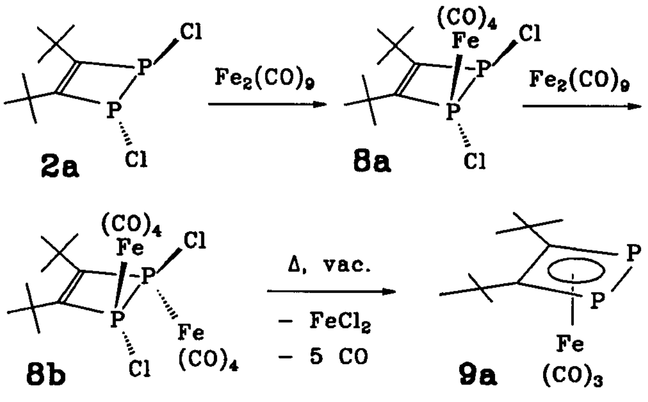


Figure 3. $^{31}P\{^{1}H\}$ NMR spectrum (109.4 MHz, THF) of the reaction products formed by a 1:1 mixture of $Fe_2(CO)_9$ and *trans*-1,2-dichloro-3,4-di-*tert*-butyl-1,2-diphosphetene (**2a**) at room temperature.

Scheme 3



If equimolar amounts of $[Fe_2(CO)_9]$ and **2a** are allowed to react, an almost statistical mixture of unreacted **2a** and the two complexes **8a** and **8b** is formed, which overall contains nearly one $Fe(CO)_4$ unit per ring ligand (Figure 3). No side products are observable. If this inseparable mixture is treated again with another mole of $[Fe_2(CO)_9]$, the remaining amounts of **2a** and primary product **8a** are both converted almost quantitatively into **8b**. An excess of $[Fe_2(CO)_9]$ therefore directly leads to good yields of pure **8b**. We interpret this finding as a proof that **8a** is an intermediate in the formation of **8b**. This means that the reactivities of the free ligand **2a** and monocomplex **8a** toward complexation by $Fe(CO)_4$ fragments are almost identical. Otherwise a preference of the formation of either **8a** or **8b** in a 1:1 reaction would have been observed, depending on the relative reactivities of **2a** and **8a**. These almost identical reactivities of a free bifunctional ligand and a corresponding monocomplex stand in contrast to the reactivity of **2b** toward reactive $[Fe(CO)_4L]$ complexes.[4]

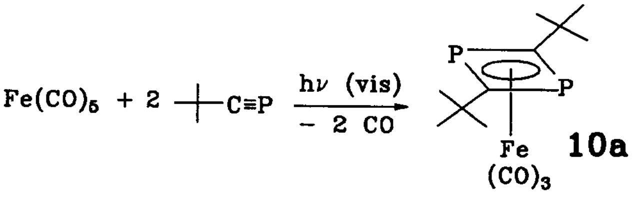
No real proof for the stereochemistry of complexes **8a** and **8b** has been found as yet since they can only be isolated as oils. All spectra of the complexes are interpreted unambiguously, if an unchanged *trans*-1,2-diphosphetene ligand structure is assumed, but this does not unequivocally rule out the corresponding cis isomer. However, the mild reaction conditions are definitely not in favor of an inversion of phosphorus(III) atoms, which are part of a ring system. Furthermore, the *trans*-diiron complex **8b** is believed to be the thermodynamically favored product.[23] There seems to be no driving force for such an isomerization process, which anyway would be expected to produce mixtures of isomers, and these have not been observed.

Reactivity of [(*trans*-1,2-Dichloro-3,4-di-*tert*-butyl-1,2-*η*-1,2-diphosphetene)(Fe(CO)$_4$)$_2$] 8b. As the dehalogenation of **2a** did not occur at room temperature even with a large excess of $[Fe_2(CO)_9]$, an intramolecular redox process was attempted to induce an interaction of the C=C double bond with at least one of the two iron atoms by heating neat **8b** in a vacuum in a kugelrohr distillation unit. The process requires heating at 190 °C, and the product [(3,4-di-*tert*-butyl-η^4-1,2-diphosphete)$Fe(CO)_3$] (**9a**) distills from the flask during the course of the heating as a pure compound, but again as an oil (Scheme 3). Thus, in contrast to carbacyclic 3,4-dichlorocyclobutene, the dechlorination of ligand **2a** in the form of its complex **8b** requires high temperatures.

To the best of our knowledge, such a dechlorination is new for P-heterocycles and is the first specific reaction leading directly to a 1,2-diphosphete complex. Only one example of such a compound is in the literature, but it was only formed together with its 1,3-isomer as an unseparable mixture.[12]

The spectra of **9a** are in complete agreement with the presence of the proposed 1,2-diphosphete ligand, but, as before, the observable spectroscopic data do not distinguish definitely between 1,2- and 1,3-regioisomers. This is even the case for the $^{13}C\{^{1}H\}$ NMR spectrum. Due to strong but, because of the symmetry of the molecule, unobservable P−P coupling (vide infra), the signals of the ring carbon atoms as well as those of the *t*-Bu groups are split into pseudo triplets, although AXY spin systems should be formed for ^{13}C-isotopomers of 1,2-isomer **9a** ($A = {}^{13}C$; $X, Y = {}^{31}P(1, 2)$ are inequivalent because of coupling with a single ^{13}C nucleus). The

Scheme 4



corresponding 1,3-isomer [(3,4-di-*tert*-butyl-η^4-1,2-diphosphete)Fe(CO)$_3$] (**10a**) is known,[24] but it also is a low-melting compound and no structural information is available. With the exception of mass spectroscopy, the spectra of **9a** and **10a** are rather different and thus they definitely are isomers. However, their main characteristics are the same. The chemical shifts of the ring nuclei, for example, are indicative for diphosphete ligands that are complexed to Fe(CO)$_3$ fragments. A good argument, but no real proof, for **10a** being a 1,3-diphosphete complex was deduced from a side product, where one phosphorus atom is complexed to a second iron atom and a small P−P coupling constant of 4.3 Hz was observed.[24] To answer the question of regioisomerism properly, we transformed both [(diphosphete)Fe(CO)$_3$] isomers, **9a** and **10a**, into crystalline compounds, utilizing the additional donor properties of the phosphorus atoms of the complexes.

Reactivity of 1,2- and 1,3-Isomers 9a and 10a of [(di-*tert*-butyl-η^4-diphosphete)Fe(CO)$_3$]. To avoid difficult-to-handle reactants or working in an autoclave, we prepared **10a** by a different route, that reported by Binger and co-workers.[24] The visible light photochemical reaction of [Fe(CO)$_5$] and *t*-BuC≡P[25] at ambient temperature in a Duran glass photolysis apparatus is quite effective (Scheme 4).

9a and **10a** both react with [Cr(CO)$_5$(THF)] at room temperature, to form mono- and diaddition products [1-η-{(3,4-di-*tert*-butyl-η^4-1,2-diphosphete)Fe(CO)$_3$}Cr(CO)$_5$] (**9b**), [1,2-η-{(3,4-di-*tert*-butyl-η^4-1,2-diphosphete)Fe(CO)$_3$}(Cr(CO)$_5$)$_2$] (**9c**), [1-η-{(2,4-di-*tert*-butyl-η^4-1,3-diphosphete)Fe(CO)$_3$}Cr(CO)$_5$] (**10b**), and [1,3-η-{(2,4-di-*tert*-butyl-η^4-1,3-diphosphete)Fe(CO)$_3$}(Cr(CO)$_5$)$_2$] (**10c**), respectively. As in the case of the addition of Fe(CO)$_4$ fragments to **2a**, the Cr(CO)$_5$ units are added step by step, and the monoaddition products **9b** and **10b** were shown to be intermediates in the formation of **9c** and **10c** by the same method (Scheme 5, Figure 4).

As for **8a**, neither **9b** nor **10b** can be prepared without giving reaction mixtures that contain all three compounds **9a**,**b**,**c** and **10a**,**b**,**c**, respectively. As a consequence, **9b** and **10b** can be observed by means of spectroscopy, but attempts to isolate them failed. NMR spectra of the FeCr complexes **9b** and **10b** present good evidence for the proposed regioisomers. Both ${}^{31}P\{{}^1H\}$ NMR spectra show the characteristics of AB spin systems. In the case of the 1,3-complex **10b** no P−P coupling is resolved, whereas the 1,2-complex **9b** exhibits a P−P coupling constant ${}^1J_{PP} = 225.7$ Hz (Figure 4). Compared with free asymmetric 1,2-diphosphetene derivatives,[1] the ${}^1J_{PP}$ constant of fully unsaturated **9b** is very large. A ${}^1J_{PP}$ of greater than 200 Hz is exactly what is required for the above-mentioned observation of pseudotriplets in the ${}^{13}C\{{}^1H\}$ NMR spectra of **9a**. In the case of **10b**, we have been able to obtain ${}^{13}C\{{}^1H\}$ NMR spectra as well. As the carbon atom signals do not split upon involving only one of the two phosphorus atoms in the formation of P−Cr bonds, an element of symmetry persists, which causes equivalence of both C-*t*-Bu units. This is possible only if **10b** contains the 1,3-diphosphete ligand.

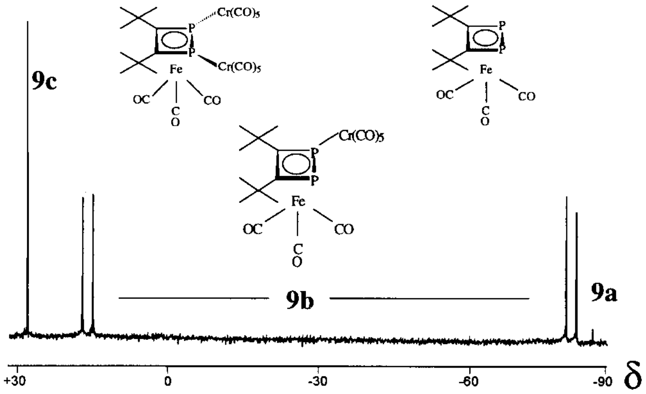
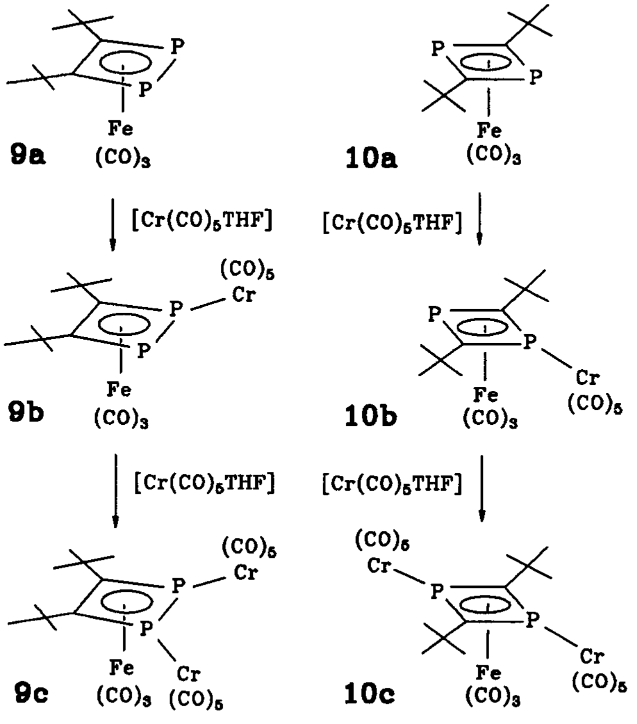


Figure 4. ${}^{31}P\{{}^1H\}$ NMR spectrum (109.4 MHz, THF) of the reaction products formed by a mixture of [Cr(CO)$_5$(THF)] and [(3,4-di-*tert*-butyl-η^4-1,2-diphosphete)Fe(CO)$_3$] (**9a**) at room temperature.

Scheme 5



X-ray Structural Investigations on 9c and 10c. As hoped, trinuclear **9c** and **10c** form good crystals which have been grown at −30 °C from a THF solution of **9c** and a solvent mixture THF/Et$_2$O in the case of **10c**. The molecular structures in the solid state are shown in Figures 5 (**9c**) and 6 (**10c**), and selected bond distances and angles are summarized in the figure captions.

In both cases, the X-ray structure analyses prove the proposed structures. The cyclic ligands are planar,

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[24] Binger, P.; Biedenbach, B.; Schneider, R.; Regitz, M. *Synthesis* **1989**, 960.

[25] Becker, G.; Gresser, G.; Uhl, W. *Z. Naturforsch.* **1981**, *36b*, 16. Optimized procedure: Rösch, W.; Hees, U.; Regitz, M. *Chem. Ber.* **1987**, *120*, 1645.

Table 1. Selected Endocyclic Bond Distances [Å] of 1,2-Diphosphete and 1,2-Diphosphetene Derivatives

	5[a]	**2a**	**11b**[b]	**9c**
C−C	1.345	1.363	1.429	1.432
C−P	1.874	1.825	1.815, 1.806	1.807, 1.825
P−P	2.115	2.189	2.175	2.147

[a] Calculated values.[13] [b] [(3,4-Di-*tert*-butyl-η^4-1,2-diphosphete)(η^8-COT)Ti].[12]

forming a trapezoid for the 1,2-diphosphete of **9c** and a rhombus for the 1,3-diphosphete of **10c**, respectively.

The length of all four P−C bonds in **10c** are essentially the same (1.78 ± 0.01 Å), and the C−P−C angles are smaller (84°) than the P−C−P angles (96°). Almost identical endocyclic bonding distances have been found also for other (η^4-1,3-diphosphete)metal complexes of the late transition metals such as cobalt[26] or in oligonuclear rhodium complexes, where a (η^4-1,3-diphosphete)Rh unit is σ-bonded to a second rhodium atom.[15] This indicates an almost complete separation of the orthogonal σ and π coordination properties of the ligand and a cyclic delocalization of the π electrons within the ring. The different covalent radii of P and C atoms cause the rhombic deformation of the otherwise ideal square of a η^4-cyclobutadiene ligand.[10,27] The situation is different only in the case of the 16-VE early transition metal complex [(2,4-di-*tert*-butyl-η^4-1,3-diphosphete)(η^8-COT)Ti] (**11a**), where alternating P−C bond lengths are observed.[12] This has been related to the calculated structural data of free unsubstituted 1,3-diphosphete **4**, which exhibits an even more pronounced parallelogram structure.[13] In contrast to the 18-VE late transition metal complexes, **11a** obviously does not allow a complete π electron delocalization within the 1,3-diphosphete ligand, probably due to a reduced back-bonding capacity of the electron-poor early transition metal center.

Such a 16-VE (COT)Ti complex is the only known example of a (η^4-1,2-diphosphete)M complex.[12] As for **9c**, a planar trapezoid is observed for the 1,2-diphosphete ligand of [(3,4-di-*tert*-butyl-η^4-1,2-diphosphete)(η^8-COT)-Ti] (**11b**), and the same is true for the calculated structure of free unsubstituted 1,2-diphosphete **5**[13] and the dichloro-1,2-diphosphetene **2a**.[16] The endocyclic bond distances of these four species have been compiled in Table 1.

The most striking fact is the very close conformity of the C−C and C−P bond lengths of **9c** and **11b**, but the P−P bond of **11b** is 0.028 Å longer than that of **9c**. The P−P bond of **11b** is therefore only 0.014 Å shorter than the P−P single bond of **2a**, and this is a value that is only slightly larger than the sum of the 3σ ranges. The influence of the metal atoms on the structural features of **9c** or **11b** can be studied, when we compare the endocyclic bond distance data of the complexes with the calculated values of the free 1,2-diphosphete **5**. Both, the C=C and P=P bonds of **5** are elongated by 0.032 (P−P of **9c**) to 0.087 Å (C−C of **9c**), but the average value of the P−C bonds of **9c** and **11b** is 0.05 Å shorter than that of **5**. On the basis of the structural data of **10c** and its interpretation, we believe we have good reasons for neglecting the influence of the Cr(CO)$_5$ fragments in the case of **9c**, too. In both cases σ- and π-bonding orbitals of the ring ligand are orthogonal and thus do not mix. The observed effects on the ring ligand therefore have to be interpreted only on the basis of π bonding of an electron-rich (Fe) or electron-poor transition metal atom (Ti). As for the 1,3-diphosphete complexes, we can explain the elongation of the P=P and C=C double bonds toward values that are between single and double bonds mainly on the basis of the donation of π electron density to the metal atom. The dominating cause of the shortening of the P−C bond length is an electron back-donation from the π-bonded metal to ligand π^* orbitals. The second effect should be smaller for the 16-VE species **11b** than it is for **11a**, but in the case of **11b** only the P−P bond is more elongated than for 18-VE complex **9c**. As a simple explanation for this effect has not been found yet, the problem seems to require a theoretical study.

Conclusions

Not only in the case of free 1,2-diphosphetene **2a** but also for the diphosphete complexes **9a** and **10a** we found experimental evidence for a stepwise addition of suitable transition metal complex fragments such as Fe(CO)$_4$ and Cr(CO)$_5$ to these bifunctional P$_2$ ligands. The finding of closely related σ ligand reactivities of the uncomplexed species as well as for their monocomplexes was assumed in the case of 1,3-diphosphete complex **10a**, as the donor orbitals point in opposite directions and the two phosphorus atoms are not bonded directly to each other. This was not expected for **2a**, as neighboring P atoms should interact to some extent and a chemical reaction of one P atom should influence the other one. The sterically favorable trans arrangement of the lone pairs is no argument against a proposed influence, as in the case of cyclotetraphosphanes, for example, no report has appeared in the literature of neighboring P atoms with a trans stereochemistry which have been both coordinated to transition metal atoms. Finally, in the case of 1,2-diphosphete complex **9a** the two P-lone pair orbitals are situated in the plane of the ring at neighboring positions, and they form an angle of ca. 100°. This can be estimated with some degree of certainty from the angle between the P−Cr bonds of complex **9c**. Consequently, the two Cr(CO)$_5$ fragments of **9c** do interact (Figure 5), as can be deduced from the positions of the equatorial carbonyl groups. To minimize the repulsion between the CO ligands of the two chromium atoms, the ligand C(53)O(53) of Cr(2) is thus positioned right in the middle between the two CO ligands C(41)O(41) and C(44)O(44) of Cr(1). In this cog-wheel-like conformation, however, only weak repulsion between the two Cr(CO)$_5$ fragments of **9c** remains, but entropy is lost.

We started our investigations with the aim of using 1,2-diphosphetene or 1,2,3-triphospholene derivatives as π,σ ligands. This point still remains open, as no stable complexes have been isolated that contain such a structural element. On the other hand, the thermally induced redox reaction of diiron complex **8b** would be difficult to understand without the possibility of developing an interaction between a P-σ-bonded iron atom

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(26) Hitchcock, P. B.; Maah, M. J.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1986**, 737. Binger, P.; Milczarek, R.; Mynott, R.; Krüger, C.; Tsay, Y.-H.; Raabe, E.; Regitz, M. *Chem. Ber.* **1988**, *121*, 637.

(27) Deeming, A. J. *Compr. Organomet. Chem.* **1982**, *4*, 459.

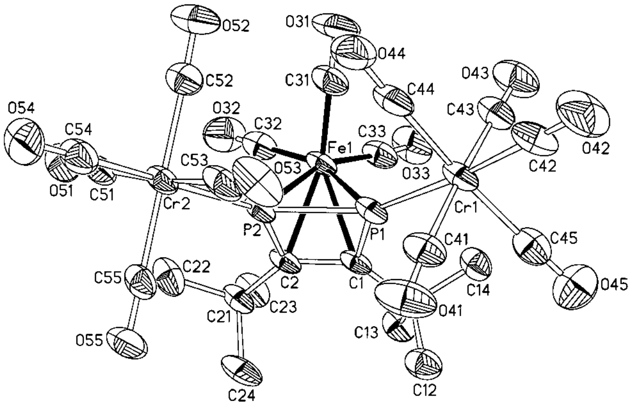


Figure 5. View of the molecular structure of [1,2-η-{(3,4-di-*tert*-butyl-η^4-1,2-diphosphete)Fe(CO)$_3$}(Cr(CO)$_5$)$_2$] (**9c**) in the solid state. Selected bond distances [Å] and angles [deg]: P(1)–C(1), 1.807(4); P(2)–C(2), 1.825(4); P(1)–P(2), 2.147(2); C(1)–C(2), 1.432(6); Fe(1)–P(1), 2.3343(14); Fe(1)–P(2), 2.3107(13), Fe(1)–C(1), 2.174(4); Fe(1)–C(2), 2.150(4); Cr(1)–P(1), 2.3501(14); Cr(2)–P(2), 3.3680(13); C(1)–P(1)-P(2), 78.7(2); C(2)–P(2)–P(1), 78.6(2); C(2)–C(1)–P(1), 102.0(3); C(1)–C(2)–P(2), 100.7(3). The hydrogen atoms are omitted for clarity.

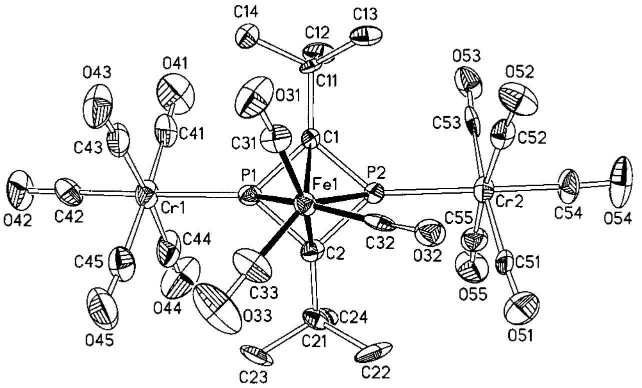
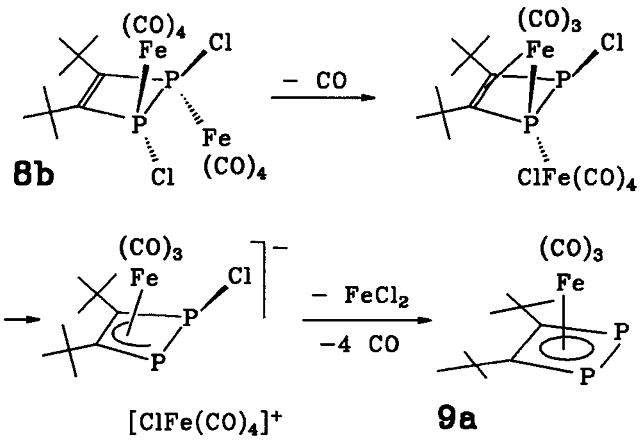


Figure 6. View of the molecular structure of [1,3-η-{(2,4-di-*tert*-butyl-η^4-1,3-diphosphete)Fe(CO)$_3$}(Cr(CO)$_5$)$_2$] (**10c**) in the solid state. Selected bond distances [Å] and angles [deg]: P(1)–C(1), 1.781(7); P(2)–C(2), 1.791(8); P(2)–C(1), 1.776(7), P(1)–C(2), 1.782(7), Fe(1)–P(1), 2.285(3); Fe(1)–P(2), 2.320(3); Fe(1)–C(1), 2.176(7); Fe(1)–C(2), 2.156(7); Cr(1)–P(1), 2.352(3); Cr(2)–P(2), 2.371(2); C(1)–P(1)–C(2), 84.0(3); P(2)–C(1)–P(1), 96.1(4); C(1)–P(2)–C(2), 83.9(3); P(1)–C(2)–P(2), 95.6(4). The hydrogen atoms are omitted for clarity.

Scheme 6



with the π electrons of the adjacent C=C double bond, most probably after loss of one CO ligand, but without breaking the Fe–P σ bond at the same time. The other iron atom would be able to insert into to its neighboring P–Cl bond. This might be the initiating step for the dechlorination of the ring ligand. Removing the first chlorine substituent with one iron atom from the ring allows the formation of an (η^3-phospaallyl)Fe unit, a molecular building block, which has been known for some time now.[28] The removal of the second chlorine atom is most probably not possible in an intramolecular reaction because of the trans stereochemistry of the involved phosphorus atoms (Scheme 6).

Up to now we have not found proof for the proposed intramolecular reaction mechanism, but this point is under current investigation. There is little reason to assume a primary attack from an external iron carbonyl complex fragment on either a P–Cl or the C=C double bond, as this would have been much easier in the case of free ligand **2a**. But **2a** is almost quantitatively converted by Fe(CO)$_4$ fragments into **8b** without any observable side reaction (Figure 3).

This new and specific route to 1,2-diphosphete complex **9a** is believed to be of more use, as **2a** should be able to react with several different transition metal complex fragments, and most of them will dechlorinate the P-heterocycle at elevated temperatures as well. We are interested in a better access to (η^4-diphosphete)M complexes, because several of these are robust compounds.[10,26,29] Therefore the coligands of such compounds in some cases may be removed without breaking the M–diphosphete bond.[16,30] As (η^4-cyclobutadiene)M or (η^4-heterocyclobutadiene)M units are identical in their electron count with an (η^5-cyclopentadienyl)M′ fragment, if M′ is the left neighbor of M in the periodic table, many useful applications can be imagined for (η^4-diphosphete)M complexes,[31] especially as we now have found access to both regioisomers.

Experimental Section

General Information. All reactions were carried out under an atmosphere of purified and dried nitrogen using Schlenk-type glassware. Solvents and starting materials were dried and saturated with nitrogen according to standard procedures.

Instruments used: ^{1}H,^{13}C NMR: JEOL-GX 270 operating at 270 MHz (^{1}H) and 67.7 MHz (^{13}C), and JEOL-JNM-LA 400 operating at 400 MHz (^{1}H) and 100.4 MHz (^{13}C), respectively; ^{31}P {^{1}H} NMR: JEOL-EX 270 (109.4 MHz), Bruker Avance DPX 300 (121.5 MHz), and JEOL-JNM-LA 400 (161.7 MHz). Mass spectra: JEOL JMS 700 (FD or EI mode, 70 eV). IR: Perkin-Elmer FT-IR Model 16. Elemental analyses were performed at the microanalytical laboratory of the Institut für Anorganische Chemie, University of Erlangen–Nürnberg. The

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[29] Driess, M.; Hu, D.; Pritzkow, H.; Schäufele, H.; Zenneck, U.; Regitz, M.; Rösch, W. *J. Organomet. Chem.* **1987**, *334*, C35. Zenneck, U. *Angew. Chem.* **1990**, *102*, 171; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 126.

[30] Böhm, D.; Knoch, F.; Kummer, S.; Schmidt, U.; Zenneck, U. *Angew. Chem.* **1995**, *107*, 251; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 198. Knoch, F.; Böhm, D.; Kummer, S.; Zenneck, U. *Z. Kristallogr.* **1995**, *210*, 801. Böhm, D.; Geiger, H.; Knoch, F.; Kremer, F.; Kummer, S.; Le Floch, P.; Mathey, F.; Schmidt, U.; Zenneck, U. *Phosphorus, Sulfur, Silicon* **1996**, *109–110*, 173.

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column chromatography material used was silica gel or neutral alumina (70−230 mesh) deactivated with 5% degassed water. Photochemical reactions have been performed with a Hg-vapor lamp, Philips HPK 125 W, in a locally constructed Duran glass apparatus, which allows temperature control and pumping of the reactant solution through the irradiation zone. For kugelrohr distillation a Büchi GKR 51 was used, which allows working between −78° and 250 °C and evacuating the apparatus to a vacuum of 0.005 mbar.

The following starting materials have been prepared as reported in the literature: *trans*-1,2-dichloro-3,4-di-*tert*-butyl-1,2-diphosphetene (**2a**),[16] 1,2,3,4,5-pentaphenyl-1,2,3-triphospholene (**3a**),[4] [(1,5-COD)$_2$Fe],[19] and P≡C-*t*-Bu.[25] All other materials have been purchased from standard commercial sources in synthetic quality.

[(1,2,3,4,5-Pentaphenyl-1,3-*η*-1,2,3-triphospholene)(Cr(CO)$_5$)$_2$] (6). A solution of $Cr(CO)_6$ (2.2 g, 10 mmol) in 150 mL of THF was irradiated for 3 h in a tap water cooled 125 W photolysis glass apparatus. The resulting solution of [Cr(CO)$_5$THF] was added to a solution of 1.8 g (3.5 mmol) of 1,2,3,4,5-pentaphenyl-1,2,3-triphospholene (**3a**) in 20 mL of THF and stirred for 12 h at room temperature. After removal of the solvent in a vacuum, excess $Cr(CO)_6$ was sublimed at 40 °C. Chromatography on silica/5% water in light petroleum ether (PE) and PE/toluene mixtures allowed the purification of the yellow product. Yield: 2.87 g (3.2 mmol, 91%). ^{1}H NMR (C_6D_6): δ 8.13−6.60 (m). ^{31}P{^{1}H} NMR (C_6D_6): δ +88.46 (d, J = 256.9 Hz); −33.96 (dd, J_1 = 253.9 Hz, J_2 = 258.4 Hz); (simulated) δ +88.46 (d); −33.95 (dd); J = −256.6 Hz. EI-MS [*m*/*z* (%)]: 886 (M$^+$, 100, isotopic pattern equals $C_{42}H_{25}Cr_2O_{10}P_3$); 858 (M$^+$ − CO, 10); 830 (M$^+$ − 2CO, 6); 802 (M$^+$ − 3CO, 3); 778 (M$^+$ − PPh, 15); 694 (M$^+$ − Cr(CO)$_5$, 40); 666 ([(C$_2$P$_3$Ph$_5$)Cr(CO)$_4$]$^+$, 13); 502 (C$_2$P$_3$Ph$_5$$^+$, 8). IR (THF): ν(CO) = 2061, 1948, 1930.

***trans*-[(1,2,3,4-Tetraphenyl-1,2-*η*-1,2-diphosphetene)(Cr(CO)$_5$)$_2$] (7a).** A solution of 1.33 g (1.50 mmol) of [(1,2,3,4,5-pentaphenyl-1,3-*η*-1,2,3-triphospholene)(Cr(CO)$_5$)$_2$] (**6**) in 100 mL of THF was irradiated for 8 h in a tap water cooled 125 W photolysis glass apparatus. After removal of the solvent in a vacuum the orange-yellow product was purifid by chromatography on silica/5% water in PE/toluene, 4:1. Yield: 200 mg (0.26 mmol, 17%). ^{1}H NMR (acetone-d_6): δ 8.22 (m); 7.75 (m); 7.49 (m); 7.42 (m). ^{13}C{^{1}H} NMR (acetone-d_6): δ 221.29 (t, J = 2.5 Hz, CO$_{trans}$); 215.72 (t, J = 5.8 Hz, CO$_{cis}$); 149.28 (t, J = 19 Hz); 136.37 (t, J = 7.4 Hz); 135.59 (t, J = 10.7 Hz); 134.16 (t, J = 7.4 Hz); 133.19 (s); 131.09 (s); 130.61; 130.60; 130.56. ^{31}P{^{1}H} NMR (C_6D_6): δ +91.37 (s). FD-MS [*m*/*z* (%)]: 694 (M$^+$, 100). Anal. Calcd for $C_{36}H_{20}CrO_{10}P_2$: C 55.54; H 2.59. Found: C 56.36; H 2.40.

[(*trans*-1,2-Dichloro-3,4-di-*tert*-butyl-1-*η*-1,2-diphosphetene)Fe(CO)$_4$] (8a) and [(*trans*-1,2-Dichloro-3,4-di-*t*-butyl-1,2-*η*-1,2-diphosphetene)(Fe(CO)$_4$)$_2$] (8b). A solution of *trans*-1,2-dichloro-3,4-di-*tert*-butyl-1,2-diphosphetene (**2a**) (186 mg, 0.69 mmol) in 30 mL of THF was added to $Fe_2(CO)_9$ (522 mg, 1.43 mmol). The reaction mixture was stirred for 24 h at room temperature. After removing the solvent in a vacuum, the brown residue was dissolved in light petroleum ether (PE) and purified by a short (3 cm) chromatography on silica/5% water. The PE was removed in a vacuum again to yield 349 mg of spectroscopically pure **8b** (0.58 mmol, 84.1%) as a red oil. ^{1}H NMR (C_6D_6): δ 1.25 (s, 18 H, *t*-Bu). ^{13}C{^{1}H} NMR (C_6D_6): δ 31.43 (s, −C(CH_3)$_3$); 39.10 (pt, −C(CH$_3$)$_3$, ^2J(P,C) + ^3J(P,C) = 14.08 Hz); 164.28 (pt, C-ring, ^1J(P,C) + ^2J(P,C) = 16.15 Hz); 212.19 (pt, C═O, ^2J(P,C) + ^3J(P,C) = 5.38 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 157.6 (s). FD-MS [*m*/*z* (%)]: 606 (M$^+$, 100, isotopic pattern equals $C_{18}H_{18}Cl_2Fe_2O_8P_2$). IR (PE): ν(CO) = 1975, 2044.

Unseparable mixtures of **2a**, **8a**, and **8b** were obtained if equimolar amounts of **2a** and $Fe_2(CO)_9$ were allowed to react in the same way. Addition of another mole of $Fe_2(CO)_9$ to the mixture and stirring for 24 h transformed **2a** and **8a** into **8b**. Data of **8a** from such a mixture, which was purified by a short chromatography (3 cm) on alumina/5% water to give a red oil: ^{1}H NMR (C_6D_6): δ 1.10 (s, 9H, *t*-Bu); 1.16 (s, 9H, *t*-Bu). ^{31}P{^{1}H} NMR (C_6D_6): δ 69.05 (d, 1P, P$_2$, J(PP) = 129.36 Hz); 120.83 (d, P$_1$, J(PP) = 129.36 Hz). FD-MS [*m*/*z* (%)]: 438 (M$^+$, 100, isotopic pattern equals $C_{14}H_{18}Cl_2FeO_4P_2$).

[(3,4-Di-*tert*-butyl-*η*^{4}-1,2-diphosphete)Fe(CO)$_3$] (9a). 8b (383 mg, 0.63 mmol) was placed in the hot zone of an evacuated kugelrohr distillation unit (0.05 mbar). After reaching 190 °C 95 mg of spectroscopically pure **9a** (0.28 mmol, 44.4%) condensed within 1 h in an ice-cooled glass bulb as a yellow oil. ^{1}H NMR (C_6D_6): δ 1.00 (s,18 H, *t*-Bu). ^{31}P{^{1}H} NMR (C_6D_6): δ −84.63 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 32.38 (pt, −C(CH_3)$_3$, ^3J(P,C) + ^4J(P,C) = 4.12 Hz); 37.45 (pt, −C(CH$_3$)$_3$, ^2J(P,C) + ^3J(P,C) = 2.91 Hz); 134.89 (pt, C-ring, ^1J(P,C) + ^2J(P,C) = 27.66 Hz); 214.18 (s, C═O). FD-MS [*m*/*z* (%)]: 340 (M$^+$, 100, isotopic pattern equals $C_{13}H_{18}FeO_3P_2$). IR (PE): ν(CO) = 1990, 2060.

[1,2-*η*-{(3,4-Di-*tert*-butyl-*η*^{4}-1,2-diphosphete)Fe(CO)$_3$}(Cr(CO)$_5$)$_2$] (9c) and [1-*η*-{(3,4-Di-*tert*-butyl-*η*^{4}-1,2-diphosphete)Fe(CO)$_3$}Cr(CO)$_5$] (9b). A water-cooled solution of $Cr(CO)_6$ (199 mg, 0.91 mmol) in 45 mL of THF was irradiated for 8 h in a tap water cooled 125 W photolysis glass apparatus. The resulting solution of [Cr(CO)$_5$THF] in THF was added to 103 mg (0.30 mmol) of **9a** and stirred for 48 h at room temperature. After removal of the solvent in a vacuum, the residue was dissolved in a few milliliters of THF and filtered through Al_2O_3/5% water. Recrystallization from THF yielded 131 mg (0.18 mmol, 60.0%) of yellow **9c**. ^{1}H NMR ($CDCl_3$): δ 1.43 (s,18 H, *t*-Bu). ^{13}C{^{1}H} NMR (C_6D_6): δ 33.25 (s, −C(CH_3)$_3$); 38.22 (pt, −C(CH$_3$)$_3$, ^2J(P,C) + ^3J(P,C) = 6.43 Hz); 126.49 (pt, C-ring, ^1J(P,C) + ^2J(P,C) = 11.90 Hz); 209.84 (s, C═O); 213.79 (pt, (C═O), ^2J(P,C) + ^3J(P,C) = 5.47 Hz); 218.89 (s, C═O). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 28.76 (s). FD-MS [*m*/*z* (%)]: 724 (M$^+$, 100). IR ($CDCl_3$): ν(CO) = 2083, 2067, 2047, 1994, 1965. Anal. Calcd for $C_{23}H_{18}Cr_2FeO_{13}P_2$: C 38.15; H 2.51. Found: C 37.48; H 2.39.

Reaction mixtures, composed of equimolar amounts of $Cr(CO)_6$ and **9a**, which were treated in the same manner, formed unseparable mixtures of **9a**, **9b**, and **9c**. Data of **9b** from a filtered solution of such a mixture: ^{31}P{^{1}H} NMR (C_6D_6): δ 16.02 (d, ^1J(P,P) = 225.70 Hz); −80.42 [d, ^1J(P,P) = 225.70 Hz]. FD-MS (70 eV) [*m*/*z* (%)]: 532 (M$^+$, 100, isotopic pattern equals $C_{18}H_{18}CrFeO_8P_2$).

[(2,4-Di-*tert*-butyl-*η*^{4}-1,3-diphosphete)Fe(CO)$_3$] (10a). A solution of $Fe(CO)_5$ (1000 mg, 5.1 mmol) in 100 mL of PE was added to P≡C-*t*-Bu (1530 mg, 15.3 mmol) in a tap water cooled 125 W photolysis glass apparatus and irradiated for 8 h. The reaction mixture was filtered through a D4 glass frit, the solvent was removed in a vacuum, and the residue was distilled in a kugelrohr distillation unit (200° → 0 °C/0.1 mbar) to yield 844 mg of pure **10a** (2.5 mmol, 49.0%). The spectroscopic data of **10a** are in good agreement with those reported in the literature.[24]

[1,3-*η*-{(2,4-Di-*tert*-butyl-*η*^{4}-1,3-diphosphete)Fe(CO)$_3$}(Cr(CO)$_5$)$_2$] (10c) and [1-*η*-{(2,4-Di-*t*-butyl-*η*^{4}-1,3-diphosphete)Fe(CO)$_3$}Cr(CO)$_5$] (10b). Preparation as reported for **9b** and **9c**: $Cr(CO)_6$ (716 mg, 3.25 mmol); 60 mL of THF; irradiation for 4 h; 369 mg (1.08 mmol) of **10a**. After removal of the solvent, the residue was dissolved in a small amount of THF and filtered through Al_2O_3/5% water, and the same volume of diethyl ether was added to the yellow solution. The product crystallized at −30 °C to yield 332 mg (0.46 mmol, 42.6%) of yellow **10c**. ^{1}H NMR ($CDCl_3$): δ 1.13 (s, 18 H, *t*-Bu). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 32.35 (t, −C(CH_3)$_3$, ^3J(C,P) = 4.52 Hz); 34.94 (t, −C(CH$_3$)$_3$, ^2J(C,P) = 3.31 Hz); 112.17 (t, C-ring, ^1J(C,P) = 28.11 Hz); 210.54 (s, C═O); 214.18 (t, C═O, ^2J(C,P) = 6.22 Hz); 217.99 (s, C═O). ^{31}P{^{1}H} NMR (C_6D_6): δ 82.11 (s). FD-MS [*m*/*z* (%)]: 724 (M$^+$, 100). IR ($CDCl_3$): ν(CO) = 2082, 2069, 2046, 1992, 1960. Anal. Calcd for $C_{23}H_{18}Cr_2FeO_{13}P_2$: C 38.15; H 2.51. Found: C 37.91; H 2.47.

Table 2. Experimental Data for the X-ray Diffraction Studies on 7a, 9c, and 10c

	7a	**9c**	**10c**
empirical formula	$C_{42}H_{20}Cr_2D_6O_{10}P_2$[a]	$C_{23}H_{18}Cr_2FeO_{13}P_2$	$C_{23}H_{18}Cr_2FeO_{13}P_2$
molar mass	862.61	724.16	724.16
T, K	200(2)	200(2)	200(2)
cryst size, mm	0.6 × 0.5 × 0.5	0.6 × 0.4 × 0.1	0.4 × 0.2 × 0.15
cryst syst	monoclinic	triclinic	othorhombic
space group	$P2_1/n$	P_11	$Pbca$
measured θ-range, deg	2.2−25.0	2.3−27.0	2.0−27.0
unit cell dimensions			
a, Å	11.779(3)	9.671(1)	14.613(7)
b, Å	22.671(5)	10.982(1)	19.709(10)
c, Å	14.425(3)	15.592(2)	20.598(9)
α, deg	90	101.48(1)	90
β, deg	91.27(2)	96.15(1)	90
γ, deg	90	113.72(1)	90
volume, Å^3	3851(2)	1453.1(3)	5932(5)
Z	4	2	8
ρ_{calc}, g cm^{-3}	1.487	1.655	1.622
abs coeff μ, mm^{-1}	0.707	1.400	1.371
abs corr	none	delta F^2[c]	none
refined params	610	443	377
$F^{(000)}$	1744	728	2912
measured reflns	8232	7409	7850
unique reflns	6751	6265	6463
obsd reflns[b]	4487	4457	1599
goodness-of-fit on F^2	1.275	1.042	0.587
R1[a]	0.0738	0.0546	0.0514
wR2 (all data)	0.2277	0.1542	0.1040
residual electron density e Å^{-3}; max, min	0.599, −0.651	0.731, −1.358	0.419, −0.532

[a] The formula represents **7a**·C_6D_6. [b] [$F_0 > 4\sigma(F)$]. [c] Program XABS2.[33]

Reaction mixtures, composed of equimolar amounts of $Cr(CO)_6$ and **10a**, which were treated in the same manner, formed unseparable mixtures of **10a**, **10b**, and **10c**. Data of **10b** from such a mixture: ^{1}H NMR (C_6D_6): δ 0.82 (s, 18 H, *t*-Bu). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 31.98 (pt, $-C(CH_3)_3$; $^3J(P,C) =$ 4.97 Hz); 34.52 (dd, $-C(CH_3)_3$, $^2J(P,C) = 2.51$ Hz, $^2J(P,C) =$ 7.18 Hz); 112.21 (dd, C-ring, $^1J(P,C) = 25.20$ Hz, $^1J(P,C) =$ 59.09 Hz); 212.44 (s, Fe−CO); 214.91 (d, Cr−CO$_{trans}$, $^2J(P,C)$ = 12.35 Hz); 218,70 (d, Cr−CO$_{cis}$, $^2J(P,C) = 3.31$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 4.80 (s); 114.81 (s). FD-MS [m/z (%)]: 532 (M$^+$, 100, isotopic pattern equals $C_{18}H_{18}CrFeO_8P_2$).

X-ray Structure Determinations. The data of all structural investigations were collected on a Siemens P4 diffractometer with Mo Kα radiation ($\lambda = 0.710\ 73$ Å) and a graphite monochromator using ω-scans. The structures were solved by direct methods and refined by full-matrix least-squares methods (SHELXTL 5.03).[32] Non hydrogen atoms were refined anisotropically; the hydrogen atoms were taken from a difference Fourier calculation and were isotropically refined in the case of **7a** and **10c**. In the case of **9c** all hydrogen atoms were geometrically positioned and allowed to ride on their corresponding carbon atoms. Their isotropic thermal parameters were tied to those of the adjacent carbon atoms by a factor of 1.5. Suitable crystals for X-ray structure analyses were obtained under the following conditions: **7a**, NMR-sample in C_6D_6, room temperature, yellow blocks; **9c**, THF, −30 °C, yellow plates; **10c**, THF/Et_2O 1:1, −30 °C, yellow blocks. The experimental data for the X-ray diffraction studies on **7a**, **9c**, and **10c** are summarized in Table 2.

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Supporting Information Available: The complete set of structural data for **7a**, **9c**, and **10c** (description of the structure determination, atomic coordinates, isotropic and anisotropic thermal factors, bond angles, distances, and ORTEP plots). This material is available free of charge via the Internet at http://pubs.acs.org.

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