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# Unprecedented triphosphinine iron interactions: Intramolecular electron transfer, reactivity round a corner, and a low-activated ring element exchange reaction

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## ABSTRACT

2,4,6-Tri-*tert*-butyl-1,3,5-triphosphinine (**7**) was combined with 1,5-COD or 2,4-di-*tert*-butyl-1,3-diphosphete to form iron  $\pi$ -complexes. The ligands of highly reactive [(2,4-di-*tert*-butyl-1,3-diphosphete)(2,4,6-tri-*tert*-butyl-1,3,5-triphosphinine)Fe] (**8**) are formed by cyclooligomerization of *tert*-butylphosphaalkyne (**3**) under the influence of the iron atom. **8** rearranges spontaneously to yield penta-*tert*-butyl-pentaphosphaferrocene (**9**) as the isolable product. An intramolecular electron transfer product [(1,5-COD)( $\eta^6$ -1,3,5-triphosphacyclohexa-2,5-diene-1,4-diyl)Fe<sup>(2+)</sup>] (**12**) is obtained with 1,5-COD. Addition of [(CO)<sub>5</sub>Cr(THF)] initiates an interligand hydrogen transfer to form [( $\eta^5$ -trihydropentale-nyl)Fe( $\mu$ ,1-3- $\eta$ -4,5,6-trihydro-1,3,5-triphosphinine)Cr(CO)<sub>5</sub>] (**13**) Extensive DFT calculations of isolated and reactive species, and several possible intermediates agree with the experimental observations and revealed for the first time a possible reaction sequence, which allows a low-activated exchange of ring elements between the ligands of sandwich complex **8** to form **9**. The process is based on the specific combination of the metal and its heterocyclic  $\pi$ -ligands. Both, singlet and triplet spin states play an important role in the process.

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## 1. Introduction

$\lambda^3$ -Phosphinine is an analogue of benzene and that accounts for a wide range of properties, including its  $\pi$ -complex chemistry, but the P-lone pair causes a distinct difference as it qualifies the P-heterocycle as a  $\sigma$ -ligand at the same time [1]. For the late transition metals, like iron for example, the  $\sigma$ -ligand property dominates strongly and [( $\eta^1$ -C<sub>5</sub>H<sub>5</sub>P)<sub>5</sub>Fe] can be isolated from the reaction of an

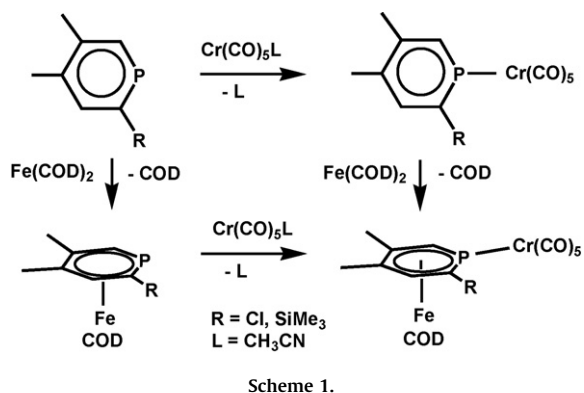
appropriate Fe-source and unsubstituted phosphinine C<sub>5</sub>H<sub>5</sub>P [2]. No trace of Fe- $\pi$ -complexes has been observed for that ligand. On the other hand, even in the absence of shielding *o*-substituents, sandwich complex [( $\eta^6$ -C<sub>5</sub>H<sub>5</sub>P)<sub>2</sub>V] is formed as the only isolable product of vanadium vapor and C<sub>5</sub>H<sub>5</sub>P again [3]. Depending on both, the size of *o*-substituents and the specific transition metal, a delicate balance of the two principal ligand properties of phosphinine and its derivatives can be stated.

In the case of iron, the coordination mode of the phosphinine depends on the co-ligands as well and  $\sigma$ - and  $\pi$ -ligand properties are almost independent from each other. (1,5-cyclooctadiene)Fe fragments form only [(1,5-COD)( $\eta^6$ -phosphinine)Fe] complexes, for *o*-Cl or SiMe<sub>3</sub>

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substituted phosphinines irrespective of additional  $\sigma$ -coordination [4] (Scheme 1).

$[(\text{Phosphinine})_n\text{Fe}(\text{CO})_m]$  complexes offer more structural options.  $\sigma$ -Coordination dominates for 2,4,6-triphenylphosphinine (**1**) as one or two may substitute CO ligands to form (2,4,6-triphenylphosphinine) $\text{Fe}(\text{CO})_4$  (**2a**) and (2,4,6-triphenylphosphinine) $_2\text{Fe}(\text{CO})_3$  (**2b**), respectively, but  $\eta^4$ -bonding adds to that in case of an occupied phosphorus lone pair.  $(\mu, \eta^4\text{-}2,4,6\text{-triphenylphosphinine})\text{-Fe}_2(\text{CO})_7$  (**2c**) was identified as an unexpected binuclear reaction product. **2a** proved to be an intermediate for the formation of **2b** as well as for **2c**. Neither a  $[(\eta^6\text{-phosphinine})\text{Fe}(\text{CO})_2]$  derivative, nor its dinuclear  $[(\mu, \eta^6\text{-phosphinine})\text{Fe}_2(\text{CO})_6]$  version has been observed [5] (Scheme 2).

If compared to hydrocarbons as arenes,  $(\eta^4\text{-arene})\text{Fe}$  complexes have been observed for naphthalene derivatives to form stable  $[(\eta^4\text{-naphthalene})\text{FeL}_3]$  complexes [6], ( $L = \text{P}(\text{OR})_3$ ;  $L_3 = \eta^6\text{-arene}$ ) but monocyclic arene ligands like benzene or toluene have been identified as  $\eta^4$ -ligands with respect to iron only in the case of highly reactive  $[(\eta^6\text{-arene})(\eta^4\text{-arene})\text{Fe}]$  species which decompose in the range of  $-50$  to  $-60^\circ\text{C}$  [7,8]. The phosphorus atom of **2c** thus causes a stabilization effect that equals that of a non-coordinated naphthalene ring with its aromatic  $\pi^6$ -electron system. The molecular structure of **2c** in the crystalline state is depicted in Fig. 1.

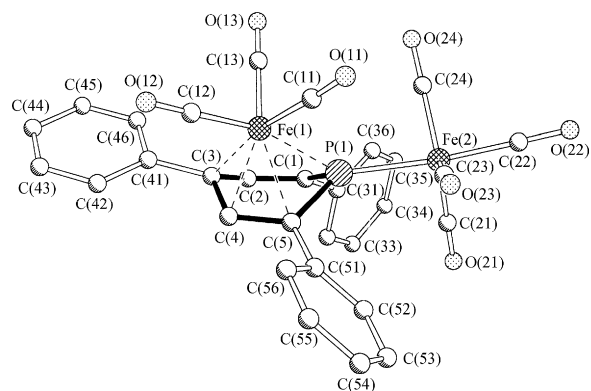
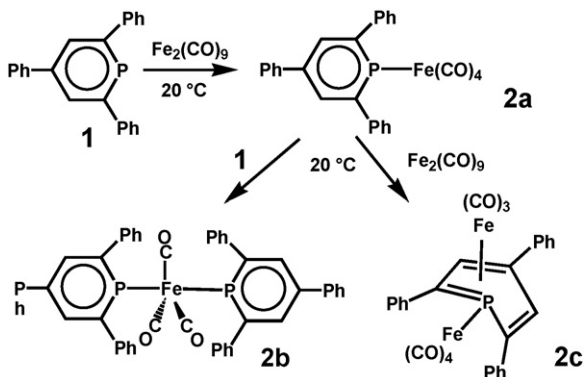
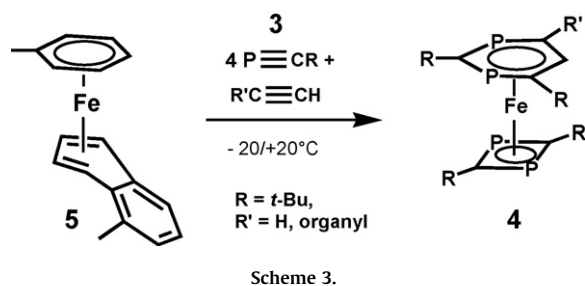


Fig. 1. Molecular structure of  $(\mu, \eta^4\text{-}2,4,6\text{-triphenylphosphinine})\text{Fe}_2(\text{CO})_7$  **2c** in the solid state. Hydrogen atoms have been omitted for clarity.

It documents a folding of the phosphinine ligand by  $46.4^\circ$  along the line  $\text{P}(1)\text{-C}(3)$ , a value slightly above the respective folding angles of  $(\eta^4\text{-naphthalene})\text{FeL}_3$  ( $L = \text{P}(\text{OMe})_3$ ,  $L_3 = \eta^6\text{-hexamethylbenzene}$ ) complexes ( $34^\circ$  and  $41^\circ$ ) [6]. This increase may be a consequence of the specific  $\sigma, \pi$ -bonding situation of the phosphorus atom and the repulsive interaction between a  $\text{Fe}(\text{CO})_4$  fragment and two *o*-phenyl phosphinine substituents. Significant  $\pi$ -electron localization within the heterocycle is indicated by alternating C–C and P–C intraring bond lengths [5].

Only one  $\lambda^3, \lambda^3$ -diphosphinine transition metal complex family appeared in the literature. It concerns  $[(\eta^4\text{-}1,3\text{-diphosphinine})(\eta^4\text{-}1,3\text{-diphosphete})\text{Fe}]$  complex class **4**, which has been formed by a  $[2 + 2 + 2]$  cyclic addition reaction of two moles of *tert*-butylphosphaalkyne (**3**), one mole of a terminal alkyne, and  $[(\eta^4\text{-}1\text{-methylnaphthalene})(\eta^6\text{-toluene})\text{Fe}]$  (**5**) as a highly reactive  $\text{Fe}(0)$  source [9] (Scheme 3). Functional alkyne substituents  $R'$  with alcohol, ester, or ether groups are tolerated. Targeted attempts to prepare  $\text{W}(\text{CO})_5$  complexes of 1,2-diphosphinines failed. Only (1,2-dihydro-1,2-diphosphinine) $\text{W}(\text{CO})_5$  derivatives have been obtained instead [10].

Based on the spectroscopic and structural features of **4**, the  $(\eta^6\text{-}1,3\text{-diphosphinine})\text{Fe}$  complexes can be regarded as prototypical (heteroarene) $\text{Fe}$   $\pi$ -complexes, but their thermal stability with a decomposition temperature around  $300^\circ\text{C}$  is remarkable. The compounds are almost as stable as ferrocene or its oligophospha analogues, but exceed the stability of most  $(\eta^6\text{-arene})\text{Fe}$  complexes with hydrocarbon  $\pi$ -ligands significantly. On the other hand, redox reactions of **4** result only in short lived ions, whereas the oxidation of its toluene complex analogue  $[(\eta^4\text{-}2,4\text{-di-tert-butyl-}1,3\text{-diphosphete})(\eta^6\text{-toluene})\text{Fe}]$  (**6**) yields a stable complex radical cation  $\mathbf{6}^+$  [11]. A preparative useful oxidative ligand decomplexation reaction of **4** by  $\text{FeCl}_3$  or  $\text{CCl}_4$  allowed the isolation of the respective free 1,3-diphosphinines as stable organophosphorus compounds. X-ray and PES spectroscopic investigations as well as MO calculations qualified them as planar benzene analogues with a significantly reduced HOMO-LUMO gap [12]. These results encouraged us to try investigating the chemistry of (1,3,5-triphenylphosphinine) $\text{Fe}$  complexes.



## 2. 2,4,6-Tri-*tert*-butyl-1,3,5-triphosphinine iron interactions

Cyclotrimerization of P-alkyne **3** should lead preferably to 2,4,6-tri-*tert*-butyl-1,3,5-triphosphinine (**7**) as the proposed thermodynamically favored aromatic  $P_3C_3R_3$  valence isomer. Some attempts of that sort appeared in the literature and resulted in surprisingly different structural motifs for the obtained complexes, including open and spirocyclic  $P_3C_3R_3$  moieties, depending on the metals used and the conditions applied [1]. Binger et al. reported about two independent routes to free **7** by cyclotrimerization of **3** in the coordination sphere of suitable (COT)Hf and amidovanadyl fragments and decomplexation of the heterocycle [13]. The first  $\eta^6$ -arene complex of **7** was obtained by reaction of an excess of P-alkyne **3** with scandium atoms. A triple decker complex was formed in small yield with two terminal ( $\eta^5$ -3,5-di-*tert*-butyl-1,2,4-triphospholyl)Sc units and a  $\mu, \eta^6: \eta^6$ -2,4,6-tri-*tert*-butyl-1,3,5-triphosphinine middle deck [14]. The availability of free **7** allowed ligand displacement reactions of some Mn, Mo, W, and Ru ( $\eta^6$ -arene)M complexes with hydrocarbon ligands to yield the related  $[(\eta^6$ -2,4,6-tri-*tert*-butyl-1,3,5-triphosphinine)ML<sub>n</sub>] complexes. They are stable compounds [15]. PES spectroscopy and DFT calculations of free **7** as well as a series of  $[(\eta^6$ -2,4,6-tri-*tert*-butyl-1,3,5-triphosphinine)M(CO)<sub>3</sub>] (M = Cr, Mo, W) complexes gave clear hints on the impact of the three phosphorus atoms on the electronic properties of the benzene ring system. Main difference of **7** and benzene is a significantly diminished HOMO – LUMO gap for **7**, which is even smaller than that of 1,3-diphosphinine. The effect concerns the  $\pi^*$ -orbitals much more strongly than the occupied  $\pi$ -orbitals. As a consequence, **7** acts as a much better  $\pi$ -acceptor ligand than benzene, but its  $\pi$ -donor capability is almost the same [12,16]. Potassium metal reduction of **7** has been reported to remove one phosphorus atom from **7** to form the related aromatic 2,4,5-tri-*tert*-butyl-1,3-diphospholyl anion, but electrochemistry revealed a quasi-reversible reduction of **7** at  $-2.315$  V vs.  $Cp_2Fe^+/Cp_2Fe$  in THF [17]. As no EPR data for the postulated anion  $7^-$  were reported, we reinvestigated the electrochemistry of **7** and determined the EPR spectroscopic properties of  $7^-$ . A reversible reduction of **7** was observed at a potential of  $-1.94$  V vs. SCE at room temperature in DME as the solvent. A reason for the differing potentials has not been found, but the redox-couple  $7/7^-$  was stable under the conditions of the experiments of this study. The experimental reduction

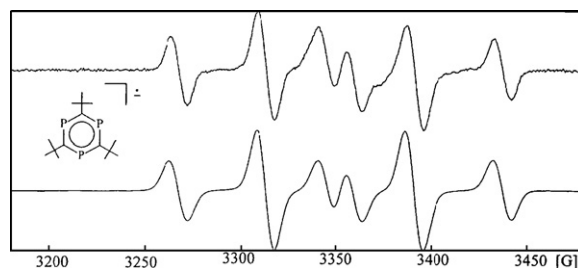


Fig. 2. X-band EPR spectrum of  $7^-K^+$  in toluene at  $-60^\circ C$  (top); ( $g$ ) = 2.0163. Simulation:  $AB_2$   $^{31}P$  hyperfine structure,  $a_A(^{31}P)$  = 77.9 G,  $a_B(^{31}P)$  = 45.7 G (bottom).

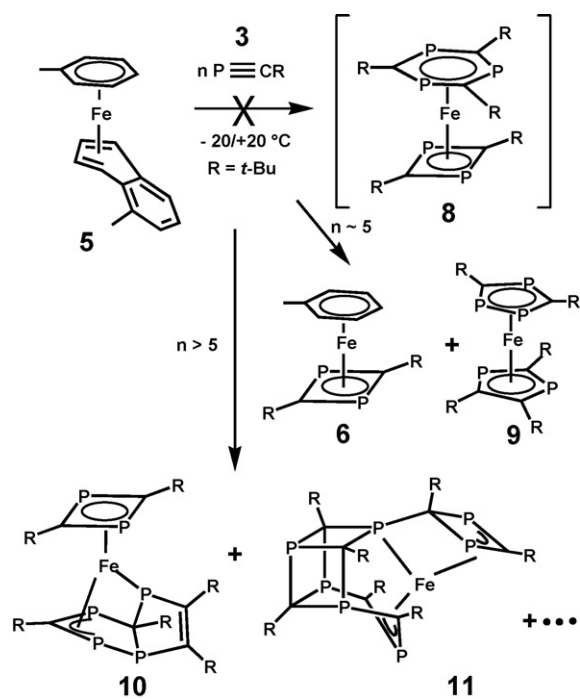
potential of **7** accounts for a dramatic anodic shift of  $+1.48$  V, if compared to that of benzene ( $-3.48$  V vs. SCE) [18]. It agrees very well with the calculated orbital energy reduction of the  $\pi^*$ -orbitals of free 1,3,5-triphosphinine  $P_3C_3H_3$  (**7a**) by just over 2 eV with respect to benzene [16]. X-band EPR spectroscopy of potassium reduced  $7^-$  in toluene proved a clean electron transfer process with the alkaline metal at low temperature too, as only one single species appeared in the spectrum with an  $AB_2$   $^{31}P$  hyperfine structure (Fig. 2).

The  $^{31}P$  hyperfine structure of  $7^-$  agrees with a single occupation of one of the degenerate  $2e''$   $\pi^*$ -orbitals [16]. A static Jahn-Teller distortion leads to the distinct differentiation of the A and  $B_2$   $^{31}P$  nuclei and causes loss of its  $C_3$ -symmetry.

Highly reactive **5** ( $T_{decomp} \sim 0^\circ C$ ) [6] was reacted with **3** in the absence of alkynes to form  $[(\eta^4$ -2,4-di-*tert*-butyl-1,3-diphosphete)( $\eta^6$ -2,4,6-tri-*tert*-butyl-1,3,5-triphosphinine)Fe] (**8**) in analogy to the formation of 1,3-diphosphinine complex **4** as the target product. **8** did not appear in the reaction mixture, but cyclodimerization product **6** and pentaphosphaferrocene derivative **9**, a valence isomer of **8**. They represent the strongly dominating main products of the reaction [11] (Scheme 4). This was a surprise, as the formation of the two five membered ring ligands of **9** requires breaking of a  $P\equiv C$  triple bond of **3** even below room temperature. All attempts to solve the problem by variation of reaction conditions or other reactive Fe(0) complexes as starting materials failed to produce **8**, but in case of an excess of **3**, novel free and iron-complexed  $P_n(CR)_m$  species appeared in the reaction mixture, most of them with cage structure [19].  $[P_6C_6R_6Fe]$  complex **10** with its bicyclic  $P_4C_4R_4$  ligand is formed in reasonable yield, but the heptamer iron complex **11** is a side product. It represents the highest oligomer of **3** reported in the literature.

18-valence electron (VE) sandwich complexes **6** and **9** are diamagnetic and robust compounds which are not easily oxidized by air contact. In contrast to that, 16 VE complexes **10** and **11** are open shell triplet species, but comparably resistant towards oxidation. Prolonged air contact of **11** resulted even in a chemoselective oxidation of the two equivalent P-atoms of the six membered ring of the cage ligand outside the 2-phosphaallyl moiety to form  $O = PR_3$  units without iron decomplexation [8].

Highly reactive 16 VE species  $[(1,5-COD)_2Fe]$  was reacted with **7** to yield  $[(1,5-COD)(2,4,6$ -tri-*tert*-butyl-

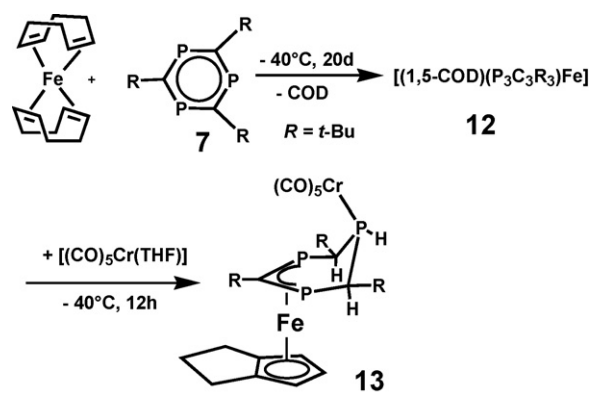


Scheme 4.

1,3,5-tri(phosphinine)Fe] (**12**) as the target product. In spite of a long reaction time of three weeks, the reaction has to be done at  $-40^\circ C$ , because the diamagnetic reaction product decomposes at room temperature to regenerate **7** and form iron slurry.  $^{31}P$  NMR spectroscopy of the cold reaction mixture revealed complete conversion of **7** into a ligand with an  $AB_2$  spin system and the parameters  $\delta_A = 1.8$ ,  $\delta_B = 5.4$ , and  $J_{AB} = 32.8$  Hz. The data point to a mirror symmetric, unsaturated  $P_3$   $\pi$ -ligand of **12** which is incompatible with a  $(\eta^6-1,3,5\text{-tri(phosphinine)Fe})$  fragment and all complexed valence isomers of **7** reported to date in the literature. It is remarkable to observe the same  $AB_2$  spin system for the three P-atoms of diamagnetic **12** and free radical **7**.

With the aim of enhancing the crystallization properties of **12** by forming a binuclear Fe–Cr  $\sigma, \pi$ -complex  $[(CO)_5Cr(THF)]$  was added at  $-40^\circ C$  after finishing the  $\pi$ -complexation step of the reaction. A stable paramagnetic reaction product **13** was isolated in small yield after chromatographic workup and recrystallization (Scheme 5). Due to non-interpretible  $^1H$  and missing  $^{31}P$  and  $^{13}C$  NMR spectra of paramagnetic **13**, only X-ray crystallography allowed identification of the binuclear complex. Besides the  $\sigma$ -bound  $Cr(CO)_5$  fragment, compound **13** contains all atoms of **12**, however, neither 1,5-COD, nor **7** were observed as ligands of  $[(\eta^5\text{-trihydropentalenyl)Fe}(\mu, 1\text{-}3\text{-}\eta\text{-}4,5,6\text{-trihydro-}1,3,5\text{-tri(phosphinine)Cr(CO)}_5)]$  (**13**) (Fig. 3).

Binuclear **13** has an electron count of 16 VE for the central Fe atom. Its paramagnetism equals that of **10** and **11**. Besides substantial differences in their coordination spheres, all three share 1,3-diphosphaallyl ligand moieties. As the ring atom connectivity of the 4,5,6-trihydro-1,3,5-tri(phosphinine) ligand of **13** is the same as that of 1,3,5-



Scheme 5.

triphosphinine **7**, there is no doubt about its origin from **7**. With the exception of the  $Cr(CO)_5$  unit, **13** appears to be a rearrangement product of thermo labile **12**. Related rearrangement processes which transform 1,5-COD by dehydrogenation into bicyclic pentalene and its derivatives have been reported in the literature. A quantitative dehydrogenation reaction of 1,5-COD to form pentalene is catalyzed at Pt-surfaces. As for the observations of this study, the process requires no heating [20]. Dehydrogenation of a cyclooctenyl ligand to form the same  $\eta^5$ -trihydropentalenyl ligand of **13** was reported for  $[(\eta^3\text{-cyclooctenyl})(\eta^4\text{-}1,5\text{-COD})Co]$  in the presence of free 1,5-COD as an intermolecular hydrogen acceptor [21]. As a consequence of forming an aromatic  $\eta^5$ -trihydropentalenyl ligand out of the isolated diene 1,5-COD, a thermodynamic driving force is assumed for that part of the process which leads to **13**. The same does not account for the threefold reduction of **7** in the coordination sphere of the iron atom, which transforms an aromatic  $\pi^6$ -system into a cyclic  $\pi^4$ -1,3-diphosphaallyl anion. As the iron atom is oxidized at the same time to form  $Fe^{2+}$ , no simplifying models can be applied to analyze the reaction which leads to **13**.

### 3. Density functional theory (DFT) calculations

Density functional theory (DFT) calculations of the compounds of this study were performed using Gaussian 98 [22] with the B3LYP hybrid functional [23]. In the case of the molybdenum complexes, the LanL2DZ basis set was used [24]. The basis set was augmented with a set of  $d$ -functions with exponents of 0.6 and 0.34 on C and P, respectively, and  $p$ -functions with exponents of 0.072 on Mo (LanL2DZP) [25]. In the case of the iron complexes, the Schäfer-Horn-Ahlrichs *split valence* basis set was used [26]. The basis set was augmented with a set of  $d$ -functions with exponents of 0.6 and 0.34 on C and P, respectively, and  $p$ - as well as  $f$ -functions with exponents of 0.098 and 1.05 on Fe and 0.086 and 0.87 on Cr (SHASvp) [25]. Due to the observation of singlet and triplet ground states for the iron complexes, both have been calculated. In the case of triplet ground states they were calculated on the basis of the *unrestricted* formalism. As B3LYP is not very precise in determining energy differences between singlet and triplet

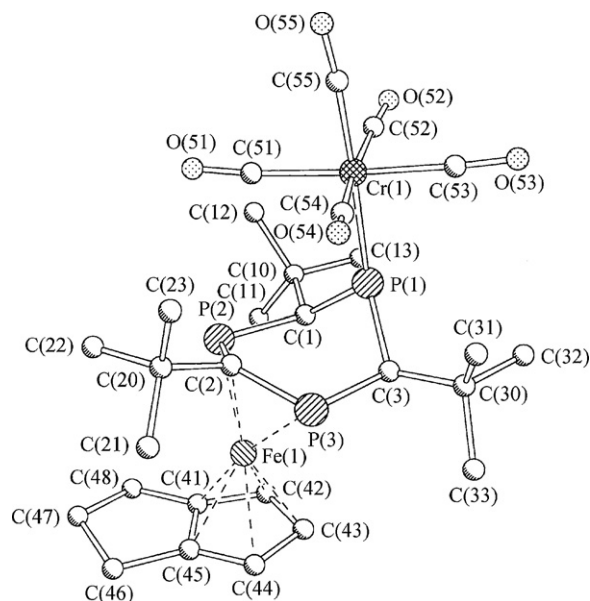


Fig. 3. Molecular structure of  $[(\eta^5\text{-trihydropentalenyl})\text{Fe}(\mu,1\text{-}3\text{-}\eta\text{-}4,5,6\text{-trihydro-}1,3,5\text{-triphosphinine})\text{Cr}(\text{CO})_5]$  **13** in the solid state. Hydrogen atoms are omitted for clarity; C(1), P(1), and C(3) carry hydrogen atoms at the ring side of the iron atom.

states, the structures were reoptimized with the B3LYP\* functional of Reiher, Salomon, and Hess [27] using the SHASvp basis set described above. To reduce the complexity of calculations, the P-heterocycles with their C-*tert*-butyl units were represented in most cases by their respective C–H analogues.

Geometry optimization of the C–H version **12a** of the proposed reaction product  $[(\eta^4\text{-}1,5\text{-COD})(1,3,5\text{-triphosphinine})\text{Fe}]$  **12** did not result in a minimum structure with a planar  $C_3$  symmetric triphosphinine ring. An alternative minimum structure **12b** with a boat shaped triphosphinine ligand was found instead. An intramolecular  $\text{Fe}(0) \rightarrow 1,3,5\text{-triphosphinine}$  two-electron transfer led to two localized  $\text{P}=\text{C}$  double bonds within a non-planar, boat-shaped ring and the formation of the  $(\eta^6\text{-}1,3,5\text{-triphosphacyclohexa-}2,5\text{-dine-}1,4\text{-diyl})\text{Fe}$  fragment of valence isomer **12b** (Fig. 4).

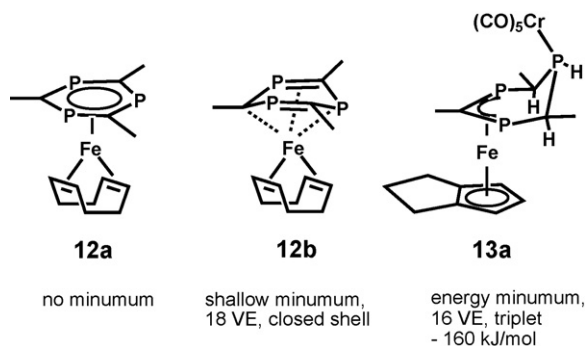


Fig. 4. B3LYP/SHASvp calculated schematic structures and energies of **12a**, **12b**, and **13a**.

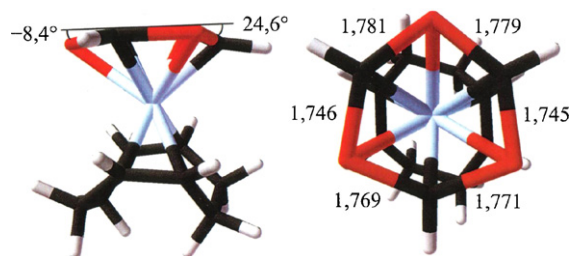


Fig. 5. B3LYP/SHASvp calculated structural parameters of **12b**.

A choice of calculated structural parameters of **12b** is given in Fig. 5. Diamagnetism, symmetry reduction of the 1,3,5-triphosphinine ligand, and the small stabilization energy of **12b** are compatible with the observation of a well-resolved  $\text{AB}_2$   $^{31}\text{P}$  NMR spectrum and thermolability of **12** at room temperature. **12** is thus believed to be  $[(\eta^4\text{-}1,5\text{-COD})(\eta^6\text{-}2,4,6\text{-tri-}t\text{-butyl-}1,3,5\text{-triphosphacyclohexa-}2,5\text{-dine-}1,4\text{-diyl})\text{Fe}]$ . In the light of that result, identity of the  $^{31}\text{P}$  spin systems of diamagnetic **12** and radical **7<sup>-</sup>** is not accidental, but reflects the single respectively double occupancy of analogous orbitals, which cause the distortions of **7<sup>-</sup>** and **12**.

This finding represents a strong contrast to the formal Ru-analogue of **12**  $[(\eta^4\text{-}1,5\text{-COD})(\eta^6\text{-}2,4,6\text{-tri-}t\text{-butyl-}1,3,5\text{-triphosphinine})\text{Ru}]$  (**14**) [15]. As for other  $(\eta^6\text{-}2,4,6\text{-tri-}t\text{-butyl-}1,3,5\text{-triphosphinine})\text{Ru}$  complexes [29], **14** appears to be a classical  $(\eta^6\text{-}1,3,5\text{-triphosphinine})\text{M}^{(0)}$  complex with a planar and  $C_3$ -symmetric heteroarene ligand. As a consequence, the iron atom of a  $(\eta^4\text{-}1,5\text{-COD})\text{Fe}$  fragment has to be regarded as significantly richer in electron density than its Ru-analogue. The incoming 1,3,5-triphosphinine ligand with its excellent  $\pi$ -acceptor properties and its low reduction potential oxidizes the iron atom to form **12** as a  $\text{Fe}^{2+}$ -complex with the dianionic  $[\text{P}_3\text{C}_3\text{R}_3]^{2-}$  ligand, but ruthenium complex **14** is composed of a  $\text{Ru}^{(0)}$  central metal and neutral ligand **7**.

Model complex **13a** appeared to be the global energy minimum among all of its isomers which were investigated. If the contribution of the  $\text{Cr}(\text{CO})_5$  fragment is eliminated, a stabilization energy of  $-152$  kJ/mol can be estimated. This is a strong driving force for the observed rearrangement process **12**  $\rightarrow$  **13**. In agreement with the experimental observations with **13**, model complex **13a** has triplet ground state with the maximum of the spin density in the vicinity of the metal atom and the diphosphallyl-unit. (Fig. 6). A mechanism for the highly complicated rearrangement process **12**  $\rightarrow$  **13** cannot be suggested in the moment, but an intramolecular mechanism is likely as all three incoming hydrogen atoms of the trihydro triphosphinine ligand are located at Fe-complexed side of the ring. The role of the  $\text{Cr}(\text{CO})_5$  moiety might be related to rehybridization of the  $\sigma$ -complexed P-atom and strong repulsive interactions with the two adjacent *o-tert*-butyl substituents of the heterocycle. Both favor ring deformation processes which are crucial for the observed rearrangement.

Theoretical evidence for a lack of stability of  $[(\eta^4\text{-}1,5\text{-COD})(\eta^6\text{-}1,3,5\text{-triphosphinine})\text{Fe}]$  **12a** and the related experimental observations for **12** led directly to the

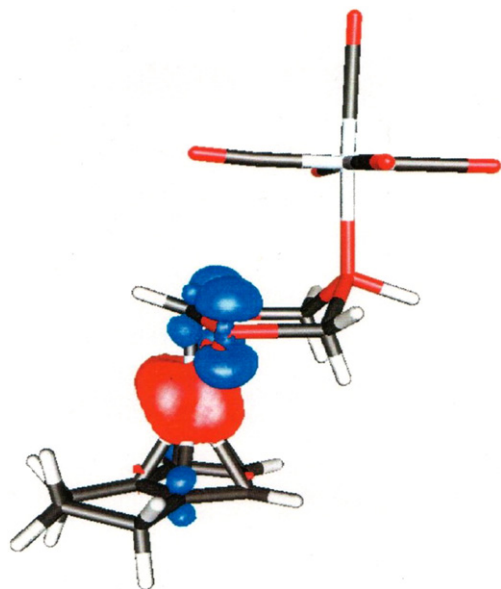


Fig. 6. B3LYP/SHAsvp calculated structure and spin density distribution of triplet complex **13a**.

question about the stability of the non-observed species **8** and to the even more interesting point, if there might exist a low-activated rearrangement process between **8** and its pentaphosphaferrocene valence isomer **9** [28]. Unlike **12b**, the C–H model compound [ $\eta^4$ -1,3-diphosphete)( $\eta^6$ -1,3,5-triphosphinine)Fe] (**8a**) forms a distinct energy minimum for a singlet species **8a(s)**, which is stabilized by  $-63.6$  kJ/mol (B3LYP\*/SHAsvp) with respect to the closest triplet state. This should be enough for isolating such a compound at room temperature, however, the influence of the *tert*-butyl substituents on the stability of **8** is not negligible and not easily to be estimated. Detailed studies which include the substituents are underway, but results are not yet available.

**8a(s)** forms a sandwich complex with a slightly boat-like distorted  $\eta^6$ -1,3,5-triphosphinine ligand but ring bending and bond length alternations are much smaller as in the case of **12a**. (Fig. 7). In a chemical sense this can be

related to the coligand 1,3-diphosphete. In contrast to 1,5-COD, it is an excellent  $\pi$ -acceptor ligand and competes with the triphosphinine for the iron 3d-electrons. This reduced iron electron density of **8a(s)** is incompatible with the specific Fe-triphosphinine interaction of **12** and the central iron atom of **8a(s)** remains in a formal zero redox state. Three related triplet structures which form local minima have been identified. One of them is structure related to the crucial intermediate for a reaction, which might be viewed as a model for a low-activated ring element exchange reaction between the two ligands of **8**. This concerns **8b(t)** with a  $\eta^4$ -triphosphinine ligand, a structural motif which is closely related to  $\eta^4$ -phosphinine complex **2c**. **8b(t)** is a candidate for significant substituent influence on the rearrangement process as the space available for them increases through ring folding. A nucleophilic attack of one of the P-lone pairs of the 1,3-diphosphete ligand on the outer carbon atom of the coordinated diene part of the  $\eta^4$ -triphosphinine ligand leads to the formation of a single P–C-bond of 197.8 pm between the two rings of triplet species **8c(t)** (Fig. 7).

The calculated molecular structure of **8c(t)** seems to be somewhat strange; however, it is isoenergetic with **8b(t)** and there exists a case of precedence. A reversible interligand bond forming process of that kind has been observed between two of the  $\pi$ -ligands of tris(2,4-*tert*-butyl-1,3-diphosphete)Mo (**15**) [30]. This specific reactivity was rationalized as a consequence of a pronounced ambiphilicity of  $\pi$ -bound unsaturated P-heterocycles. DFT calculations of methyl derivative **15a** yielded a  $C_s$ -symmetric structure as the ground state with an interligand P–C bond length of 201 pm. The calculated structural data of **15a** are closely related to the low-temperature X-ray data of **15**. (Fig. 8).  $C_{2v}$ -symmetric structure **15a'** with its three independent 1,3-diphosphete ligands represents the transition state for a reversible bond formation between the top 1,3-diphosphete ligand and one of the two other ones. This type of structure was assumed as the ground state of **15**, when the compound was prepared for the first time [31]. **15a** is stabilized by  $-14.6$  kJ/mol (B3LYP/LanL2DZP) with respect to transition state **15a'**. Calculations with hydrogen substituents of the 1,3-diphosphete ligands, led to the same principal structures, but the activation energy is reduced to only 2 kJ/mol for the

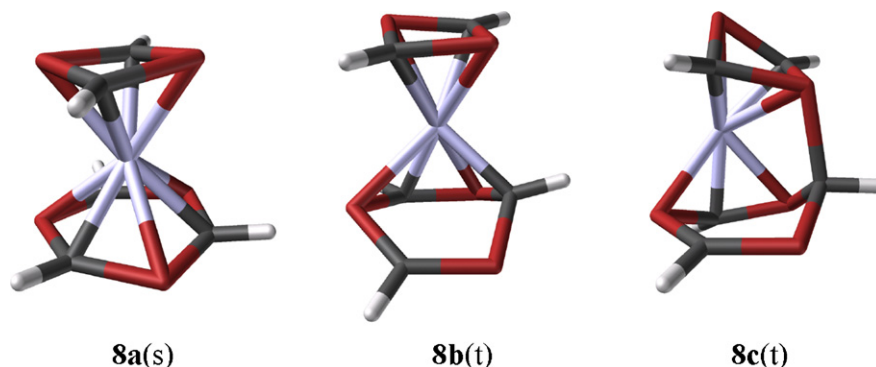


Fig. 7. B3LYP\*/SHAsvp calculated ground state structures of singlet ground state [ $\eta^4$ -1,3-diphosphete)( $\eta^6$ -1,3,5-triphosphinine)Fe] **8a(s)**, intermediate triplet state **8b(t)** ( $E_{\text{rel}}$ : 79.6 kJ/mol), and the rearrangement triplet species **8c(t)** ( $E_{\text{rel}}$ : 78.7 kJ/mol).

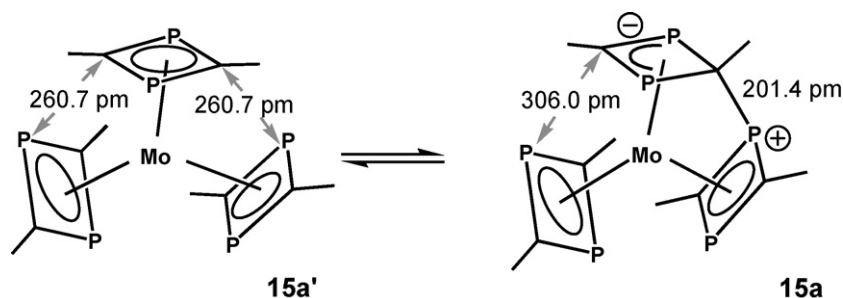


Fig. 8. Schematic drawings of the B3LYP/LanL2DZP calculated ground state of **15a** and the transition state **15a'** for the reversible interligand bond formation reaction of tris(2,4-dimethyl-1,3-diphosphete)Mo **15a**.

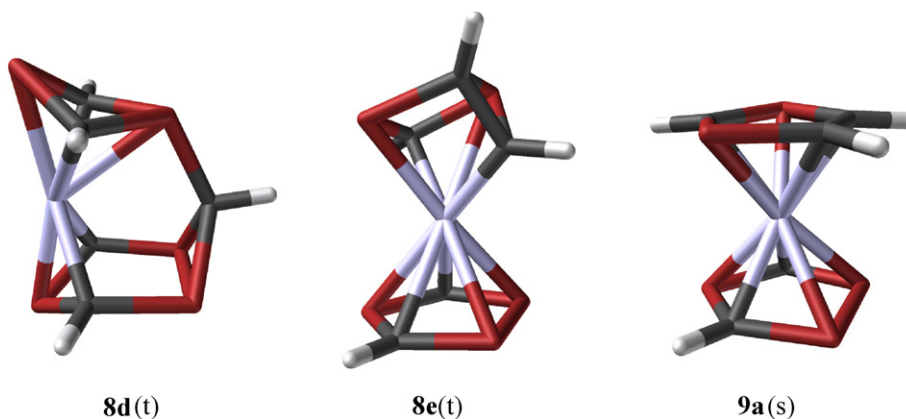


Fig. 9. B3LYP\*/SHASvp calculated ground state structures of **8d(t)** ( $E_{\text{rel}}$ : 64.9 kJ/mol), **8e(t)** ( $E_{\text{rel}}$ : 43.5 kJ/mol) and pentaphosphaferrocene **9a(s)** ( $E_{\text{rel}}$ : -210.2 kJ/mol).

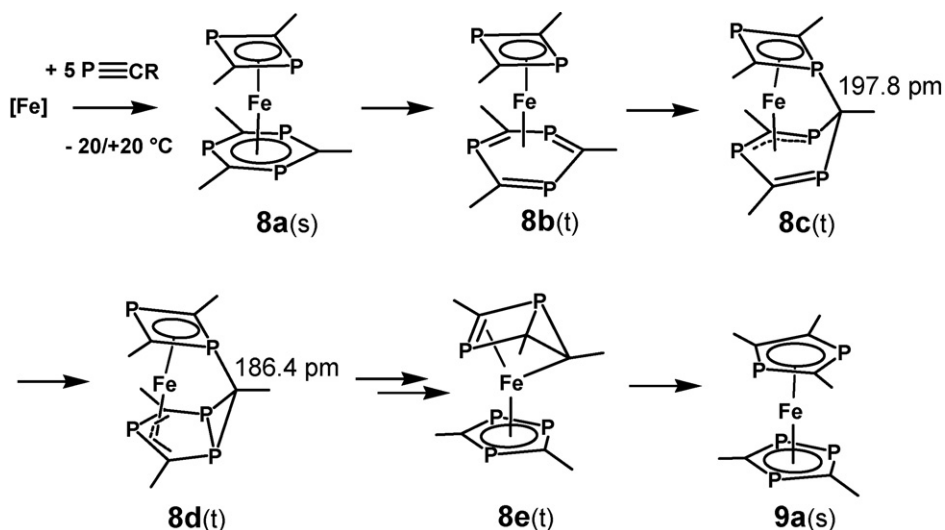
exchange process. Methyl substituent added thus more than 12 kJ/mol to the energetic differentiation of the two states **15a** and **15a'**, the contribution of the *tert*-butyl substituents of **15** is definitely bigger.

Next suggested step for the rearrangement of **8a(s)** leads to **8d(t)** by formation of a bicyclic  $\text{P}_3\text{C}_3\text{H}_3$  ligand. (Fig. 9). It exhibits a  $\pi$ -bound 2-phosphaallyl moiety and a shortened interligand P-C bond length of 186.4 pm. Formation of a bicyclic ligand releases some of the strain of **8c(t)**. This is reflected by gaining -13.8 kJ/mol relative energy with this step. Additional -21.4 kJ/mol are released when **8d(t)** is transformed into **8e(t)** by breaking two P-C bonds of the three membered ring of **8d(t)** and forming the bicyclic  $\text{P}_3\text{C}_2\text{H}_2$  ligand of **8e(t)**. This part of the rearrangement cannot proceed in a single step, but no meaningful intermediates have been located in-between these two species. Opening the internal P-C bond of **8e(t)** finishes the rearrangement reaction with the formation of pentaphosphaferrocene **9a(s)** and releasing its relative energy of -210.2 kJ/mol with respect to **8a(s)**. The calculated structure parameters of **9a(s)** and its diamagnetism agree very well with the experimental data of **9**, if the *tert*-butyl substituents are taken into consideration [11,32]. We regard this as a good test for the applied model.

The complete rearrangement process can be rationalized by the schematic drawings of Scheme 6. **8a(s)** - **8d(t)** can be regarded as formal  $\text{Fe}^{(0)}$  complexes, but **8e(t)** and

**9a(s)** are  $\text{Fe}^{2+}$  compounds with two anionic ligands. It seems to be worth mentioning, that the majority of the complicated rearrangement process takes place in the regime of the triplet states. The specific iron-P-heterocycle interaction grants a low singlet - triplet activation energy in most cases. As only 16 VE are required for the triplet species, the intermediates gain structural flexibility if compared to the related singlet 18 VE states. That helps adopting the necessary structural changes from intermediate to intermediate. A point of concern remains in the moment. The first step that converts **8a(s)** into **8b(t)** seems to be relatively high in energy for a reaction, which takes place for its *tert*-butyl derivative around or even below room temperature, but the influence of the substituents is under investigation. The structural and electronic flexibility of complexes that contain iron atoms and unsaturated P-heterocycles or P-alkynes seems to be almost unlimited in the light of these studies.

Complex **8c(t)** exhibits an open side of the molecule that should be suitable for reactions with additional ligands and its 16 VE count points to the same direction. In the case of an excess of P-alkyne **3** with respect to the iron source **5**, **3** will definitely attack **8c(t)** if it is present in solution at all. This consideration was followed by the same theoretical methods as outlined above [28]. As suggested, a P-alkyne binds side on at the iron atom of **8c(t)** to form **16a(t)**. This initiates a cage forming process. Two

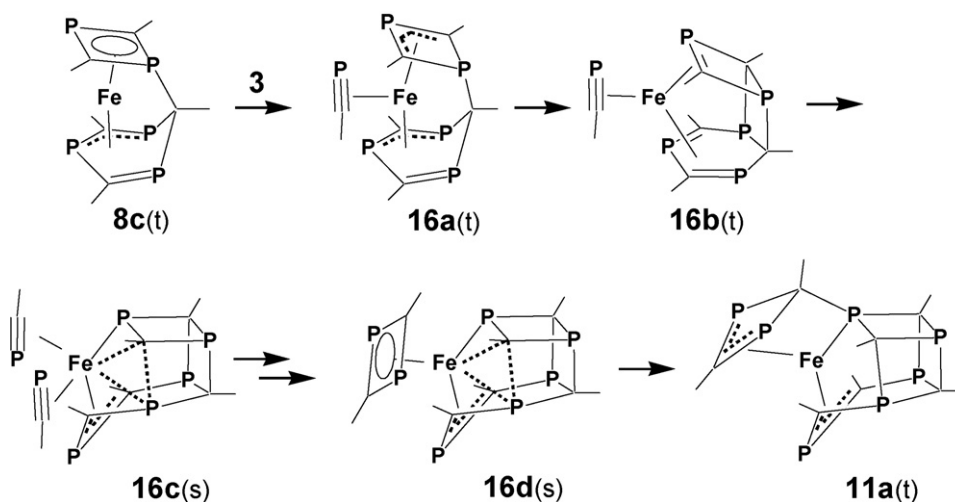


Scheme 6.

antiparallel P–C single bonds connect the former four and six membered ring ligands of **16b(t)** and squeeze the iron metal atom out of the central position between these rings. This process generates extra space in the coordination sphere of the metal atom for adding another P-alkyne. Additional electron density from the P-alkynes allows the metal to move further out of the cage in construction. The triphosphacyclohexa-1,3-diene moiety of **16b(t)** rearranges in a way that generates a  $\pi$ -complexed 2-phosphaallyl unit of **16c(s)**. Cyclic addition of the two P-alkyne ligands of **16c(s)** requires two principal steps to yield the 1,3-diphosphete ligand of **16d(s)** without significant changes of the  $\text{Fe}(\text{P}_5\text{C}_5\text{H}_5)$  cage fragment structure. The final step of the reaction sequence deals with an nucleophilic attack of a P-lone pair on a C–H unit of the 1,3-diphosphete ligand to finish with the formation of the C–H version **11a(t)** of PCR-heptamer iron complex **11** (Scheme 7). This step is just a reversed version of the

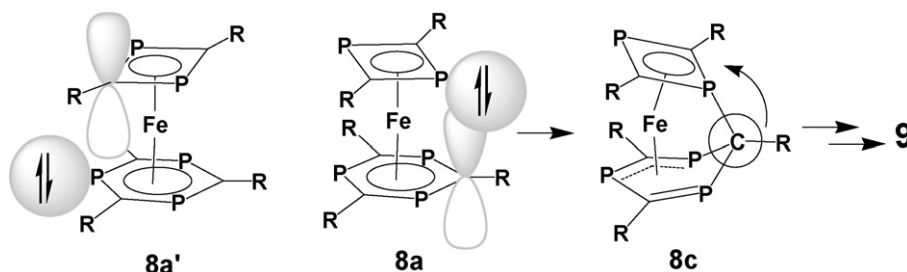
interligand P–C bond formation step **8b(t)**  $\rightarrow$  **8c(t)**, where the 1,3-diphosphete ligand played the role of the nucleophile.

As observed for the rearrangement reaction **8a(s)**  $\rightarrow$  **9a(s)**, singlet and triplet states play a role for the addition of two P-alkynes to intermediate **8c(t)** to form **11a(t)** in the end. For **16a**, the triplet state **16a(t)** is stabilized by  $-7.1$  kJ/mol with respect to its singlet analogue **16a(s)**, **16b(t)** is stabilized by  $-29.3$  kJ/mol, **16c(s)** by  $-2.9$  kJ/mol, **16d(s)** by  $29.7$  kJ/mol, and the final product **11a(t)** is stabilized by  $-33.5$  kJ/mol with respect to **11a(s)**. After correction for the additional two P-alkyne units, a relative stabilization energy of  $-205.6$  kJ/mol was determined for **11a(t)** with respect to **8a(s)**. As a consequence, **11a(t)** has to be viewed as almost isoenergetic with pentaphosphaferrocene **9a(s)**. That explains the pronounced thermal and oxidative stability of **11**, which allows even P-oxidation without decomplexation of the



Scheme 7.





Scheme 8.

metal or significant structural changes with the exception for the two additional oxygen atoms. The calculated structural parameters of molecular **11a(t)** are close to the experimental X-ray data of **11** if the different substituents are taken into consideration [19]. This demonstrates the quality of the model applied even for the triplet states.

The rearrangement reaction sequence **8a(s)** → **9a(s)** and the formation of **11a(t)** are directly linked by the common intermediate **8c(t)**. Besides the relative concentrations of iron starting material **5** and P-alkyne **3**, the relative activation energies for the competing steps **8c(t)** → **8d(t)** and **8c(t)** → **16a(t)** control the access to the two reaction channels. The activation energies have not been determined for the model compounds, but the relative energies of **16a(t)** and **8d(t)** are in favor with  $-40.6$  kJ/mol for **16a(t)** after correction for their different composition. If this relation would account for the experimental accessible *tert*-butyl derivatives, a significant preference for the formation of heptamer complex **11** would have resulted. Experiments prove the contrary. Pentaphosphaferrocene **9** dominates strongly. Again, the non-negligible influence of the *tert*-butyl substituents will contribute their part to that. On the other hand, the extensive DFT calculations allowed connecting so different structures as **9** and **11** to a common part of the complex reaction sequences that lead to the final products.

#### 4. Conclusions

What can be concluded from these combined experimental and theoretical studies? Chemical reactions between 2,4,6-tri-*tert*-butyl-1,3,5-triphosphinine **7** or its precursor compound *tert*-butylphosphaalkyne **3** with reactive  $\text{Fe}^{(0)}$  complexes resulted in completely unexpected products, which found explanation only after very deep theoretical studies. First of all, the combination of **7** as an excellent  $\pi$ -acceptor with an electron-rich  $\text{Fe}^{(0)}$  creates a unique situation for the electronic balance between these two components. Either a complete intramolecular electron transfer  $\text{Fe} \rightarrow$  triphosphinine occurs, or the  $\pi$ -bound triphosphinine is activated by the metal to open the gate to a totally unexpected reactivity, that includes the exchange of ring elements between two parallel oriented P-heterocyclic  $\pi$ -ligands of a sandwich complex. As the results of advanced DFT calculations are not directly helpful for experimental chemists to understand such a process in a sense, which allows transformation of the gained knowledge into a concept for further studies, a

closer view on the crucial steps of the reaction sequence that rearranges the proposed intermediate  $[(\eta^4\text{-}2,4\text{-di-}i\text{tert-butyl-}1,3\text{-diphosphete})(\eta^6\text{-}2,4,6\text{-tri-}i\text{tert-butyl-}1,3,5\text{-triphosphinine})\text{Fe}]$  **8** to form hexaphosphaferrocene **9** as the thermodynamically stable end product seems to be helpful.

As indicated by our earlier studies, a nucleophilic attack of a P-lone pair of one  $\pi$ -ligand on the electrophilic centers of the other P-heterocyclic  $\pi$ -ligand is reasonable [30]. Chemical reactivity of a P-lone pair of a coordinated unsaturated P-heterocycle far outside its main direction has been identified in more cases [33] and can be related to its high s-character which grants sufficient nucleophilicity of the lone pair in a wide range of angles around the P-atom. Due to different ring sizes, a P-lone pair of the 1,3-diphosphete ligand may overlap with the  $\pi^*$ -orbitals at the positions of all ring elements of the 1,3,5-triphosphinine ligand of **8a**, depending on the conformational state of the complex. That includes the phosphorus atoms but P-P interligand interaction would cause a closer contact between the *tert*-butyl substituents of the two ring ligands. This orientation is therefore regarded as a competing process with a higher activation barrier. The version the other way round, where a P-lone pair of the 1,3,5-triphosphinine acts as a nucleophile with respect to the 1,3-diphosphete ligand (**8a'**) does not work at all. The radius of the cyclic  $\pi$ -electron system of the 1,3-diphosphete ligand is smaller than that of the  $\pi$ -bound 1,3,5-triphosphinine and cannot be reached by the P-lone pairs of that ligand. (Scheme 8). As we learned from the calculations, the formation of the interligand P-C bond after converting **8a(s)** into **8c(t)** represents the crucial step for removing a CR fragment from the 1,3,5-triphosphinine and integrating it into the 1,3-diphosphete to form the 1,3-diphospholyl and 1,2,4-triphospholyl ligands of **9a**, respectively.

As a general essence of this study, we can state that a P-lone pair of the 1,3-diphosphete ligand may act like a harpoon to hit a CR fragment of the 1,3,5-triphosphinine, pull it out of the ring, and integrate it into its own structure.

#### Acknowledgements

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.crci.2010.05.023](https://doi.org/10.1016/j.crci.2010.05.023).

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