Binuclear Phospholyl Iron Carbonyls: The Limited Role of the Phosphorus Atom in Metal Complexation

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Abstract

The structures and thermodynamics of the binuclear phospholyliron carbonyls $(C_4H_4P)_2Fe_2(CO)_n$ ($n = 6, 5, 4, 3, 2$) have been investigated using density functional theory. The low-energy $(C_4H_4P)_2Fe_2(CO)_n$ ($n = 4, 3, 2$) structures are found to have direct iron-iron bonds and terminal five-electron donor pentahapto η^5 - C_4H_4P rings with the phosphorus lone pairs not involved in the bonding to the iron atoms. They are thus analogous to the corresponding cyclopentadienyliron carbonyl derivatives. However, they differ from the binuclear phospholyl manganese carbonyls $(C_4H_4P)_2Mn_2(CO)_n$ ($n = 5, 4$) for which structures with bridging seven-electron donor η^5, η^1 - C_4H_4P phospholyl rings are the lowest energy structures by substantial margins. Partially bonded phospholyl rings, as well as direct Fe-Fe bonds, are found in the carbonyl-rich $(C_4H_4P)_2Fe_2(CO)_n$ ($n = 6, 5$) species. The pentacarbonyl $(C_4H_4P)_2Fe_2(CO)_5$ does not appear to be a viable species since it is disfavored relative to CO loss and to disproportionation into $(C_4H_4P)_2Fe_2(CO)_6 + (C_4H_4P)_2Fe_2(CO)_4$.

1. Introduction

The chemistry of cyclopentadienyliron carbonyls dates back 60 years to the synthesis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ by Piper and Wilkinson in 1956 from the thermal reaction of $\text{Fe}(\text{CO})_5$ with cyclopentadiene dimer at $\sim 130^\circ\text{C}$ [1]. Subsequently both *cis* and *trans* stereoisomers of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ were separated and structurally characterized by X-ray crystallography [2, 3, 4].

Interesting species have been obtained by decarbonylation of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$. Photolysis under mild conditions gives the unsaturated $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\mu\text{-CO})_3$ [5, 6, 7], which is of interest as a stable triplet spin state metal carbonyl derivative. X-ray crystallography of the permethylated derivative $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Fe}_2(\mu\text{-CO})_3$ indicates a short $\text{Fe}=\text{Fe}$ distance of 2.265 Å, interpreted to be the formal double bond required to give each iron atom the favored 18-electron configuration [8]. Further decarbonylation of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ by prolonged pyrolysis at $\sim 100^\circ\text{C}$ leads to the tetranuclear cluster $(\eta^5\text{-C}_5\text{H}_5)_4\text{Fe}_4(\mu_3\text{-CO})_4$ containing a central Fe_4 tetrahedron with each face capped by a carbonyl group [9]. Theoretical studies on $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_n$ ($n = 4, 3, 2$) derivatives [10] suggest the formation of this cluster by dimerization of an unsaturated doubly bridged $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\mu\text{-CO})_2$ with a short $\text{Fe}\equiv\text{Fe}$ distance of ~ 2.13 Å consistent with the formal triple bond required to give each iron atom the favored 18-electron configuration.

The analogy between a bare phosphorus atom and a CH moiety [11] makes the phospholyl (phosphacyclopentadienyl) ligand, $\eta^5\text{-C}_4\text{H}_4\text{P}$, an analogue of the cyclopentadienyl ligand. Because of synthetic challenges, development of phospholylmetal chemistry lagged considerably behind the development of cyclopentadienylmetal chemistry. However, Mathey and coworkers [12, 13] used the thermal reaction of P-phenylphosphole with $\text{Mn}_2(\text{CO})_{10}$ to synthesize phospholylmanganese tricarbonyl $(\eta^4\text{-C}_4\text{H}_4\text{P})\text{Mn}(\text{CO})_3$. Comparison of the properties of $(\eta^5\text{-C}_4\text{H}_4\text{P})\text{Mn}(\text{CO})_3$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ showed that substitution of one of the CH moieties in the five-membered ring with a phosphorus atom leads to very little change in physiochemical properties such as color, odor, melting point, solubility, elution rate, and reactivity with electrophiles. However, the lone pair remaining on the phosphorus atom in the phospholyl ring makes $(\eta^5\text{-C}_4\text{H}_4\text{P})\text{Mn}(\text{CO})_3$ a ligand to a second transition metal to form a binuclear metal complex. Thus in a binuclear derivative a phospholyl ligand can act as a seven-electron donor bridging ligand across a central M_2 or MM' unit by using the phosphorus lone pair electrons in addition to the five π -electrons of the phospholyl ring (Figure 1). This possibility of a phospholyl ligand acting as a seven-electron donor

bridge across an M_2 unit suggested that binuclear phospholyl metal carbonyls might have significantly different chemistry than the corresponding cyclopentadienyl metal carbonyls.

Figure 1. The phospholyl ligand as a five-electron and a seven-electron donor in transition metal complexes.

In previous papers we have used density functional theory to investigate the mononuclear and binuclear phospholylmetal carbonyls of the transition metals manganese and cobalt of odd atomic number. For manganese the lowest energy $(\text{C}_4\text{H}_4\text{P})_2\text{Mn}_2(\text{CO})_5$ and $(\text{C}_4\text{H}_4\text{P})_2\text{Mn}_2(\text{CO})_4$ structures by a wide margin were found to have one and two seven-electron donor bridging $\eta^5,\eta^1\text{-C}_4\text{H}_4\text{P}$ phospholyl rings, respectively, thereby avoiding the need for an Mn-Mn bond to give each manganese atom the favored 18-electron configuration [14]. However, the lowest energy structure for the tricarbonyl $(\text{C}_4\text{H}_4\text{P})_2\text{Mn}_2(\text{CO})_3$ is a triply bridged $(\eta^5\text{-C}_4\text{H}_4\text{P})_2\text{Mn}_2(\mu\text{-CO})_3$ structure with terminal five-electron donor $\eta^5\text{-C}_4\text{H}_4\text{P}$ phospholyl rings in which their phosphorus external lone pairs are not involved in the manganese-ligand bonding. This $(\eta^5\text{-C}_4\text{H}_4\text{P})_2\text{Mn}_2(\mu\text{-CO})_3$ structure is analogous to that of the stable compound $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Mn}_2(\mu\text{-CO})_3$, shown by X-ray crystallography to have a very short $\text{Mn}\equiv\text{Mn}$ distance corresponding to the formal triple bond required to give each manganese atom the favored 18-electron configuration.[15]

The binuclear phospholylcobalt carbonyls were found to be very different from the phospholylmanganese carbonyls in not having seven-electron donor bridging $\eta^1,\eta^5\text{-C}_4\text{H}_4\text{P}$ rings in their energetically favored structures [16]. Thus the lowest energy $(\text{C}_4\text{H}_4\text{P})_2\text{Co}_2(\text{CO})_n$ ($n = 3, 2, 1$) structures were all found to have five-electron donor terminal $\eta^5\text{-C}_4\text{H}_4\text{P}$ rings rather than seven-electron donor bridging $\eta^5,\eta^1\text{-phospholyl}$ rings. In fact these lowest energy $(\text{C}_4\text{H}_4\text{P})_2\text{Co}_2(\text{CO})_n$ ($n = 3, 2, 1$) structures were found to be completely analogous to the isoelectronic phosphorus-free structures $(\text{C}_5\text{H}_5)_2\text{Co}_2(\text{CO})_n$ ($n = 3, 2, 1$), which have been synthesized [17, 18] and studied by density functional theory [19]. In addition, higher energy $(\text{C}_4\text{H}_4\text{P})_2\text{Co}_2(\text{CO})_n$ ($n = 3, 2, 1$) structures were found in

which the phospholyl ligand acts as a five-electron donor η^5, η^1 -C₄H₄P ligand across a Co–Co bond (Figure 1).

This paper presents a theoretical study of the phospholyl metal carbonyl derivatives of iron, as a representative transition metal of even atomic number. Even though phospholyl iron carbonyls have not yet been synthesized, iron was chosen for this study to provide a comparison of the (C₄H₄P)₂Fe₂(CO)_{*n*} (*n* = 4, 3, 2) derivatives with their extensively studied cyclopentadienyl derivatives (C₅H₅)₂Fe₂(CO)_{*n*} (*n* = 4, 3, 2) as noted above. A possible synthetic entry into these species would be reactions of one equivalent of a phospholyl anion with the readily available Fe(CO)₄I₂ to give a phospholyliron carbonyl iodide such as the unsubstituted (C₄H₄P)Fe(CO)₂I. Reductive deiodination of such species could then provide the binuclear (C₄H₄P)₂Fe₂(CO)₄ analogous to (η^5 -C₅H₅)₂Fe₂(CO)₄.

2. Theoretical Methods

Electron correlation effects were considered by employing density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds [20, 21, 22, 23, 24, 25, 26]. Thus two DFT methods were used in this study. The first method uses the B3LYP hybrid functional, which combines the three-parameter Becke functional (B3) with the Lee–Yang–Parr (LYP) generalized gradient correlation functional [27, 28]. The other DFT method used in the present paper is BP86, which combines Becke’s 1988 exchange functional (B) with Perdew’s 1986 gradient corrected correlation functional method (P86) [29, 30].

The B3LYP and BP86 methods agree with each other fairly well in predicting the structural characteristics of the (C₄H₄P)₂Fe₂(CO)_{*n*} derivatives of interest. However, the B3LYP and BP86 methods predict quite different singlet-triplet splittings. This is not unusual, since Reiher and collaborators [31] have found that the B3LYP predictions always favor the high-spin state whereas the BP86 prediction favors the low-spin state, with the true value lying between the B3LYP and BP86 predictions. For this reason, they proposed a new parametrization for the B3LYP functional, namely B3LYP*, which provides electronic state orderings in closer agreement with experiment. These same authors also tested this B3LYP* functional with the G2 test set and obtained satisfactory results [32]. In the present paper, since the B3LYP and BP86 methods predict different singlet-triplet splittings, we also used the B3LYP* method to give more reliable energy differences between the singlet and triplet structures as well as more reliable dissociation energies.

The present report lists the values from all three DFT methods. For the $\nu(\text{CO})$ vibrational frequencies, the B3LYP method usually predicts higher values than the BP86 method by $\sim 100 \text{ cm}^{-1}$. Previous work shows that the BP86 results are closer to the experimental $\nu(\text{CO})$ values without using any scaling factors [33,34]. This concurrence may be accidental, since the theoretical vibrational frequencies predicted by BP86 are harmonic frequencies, whereas the experimental fundamental frequencies are anharmonic.

All computations were performed using the double- ζ plus polarization (DZP) basis sets. The DZP basis sets used for carbon and oxygen add one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(\text{C}) = 0.75$ and $\alpha_d(\text{O}) = 0.85$ to the standard Huzinaga–Dunning contracted DZ sets [35, 36] and are designated (9s5p1d/4s2p1d). The DZP basis set used for phosphorus adds one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(\text{P}) = 0.60$ to the standard Huzinaga–Dunning contracted DZ sets and are designated (12s8p1d/6s4p1d). For hydrogen, a set of p polarization functions $\alpha_p(\text{H}) = 0.75$ is added to the Huzinaga–Dunning DZ set. The loosely contracted DZP basis set for iron is the Wachters primitive set [37] augmented by two sets of p functions and a set of d functions, contracted following Hood, Pitzer, and Schaefer [38], designated (14s11p6d/10s8p3d).

The geometries of all structures were fully optimized using **all three DFT** methods. The vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities were also evaluated analytically. All of the computations were carried out with the Gaussian 09 program [39], exercising the fine grid option (75 radial shells, 302 angular points) for evaluating integrals numerically [40].

3. Results and Discussion

3.1 Molecular Structures

3.1.1 $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_4$. Eight low-energy structures were found for $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_4$; all of these structures are singlets (Figure 2). Triplet $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_4$ structures were also found. However, they are not discussed in this paper since the lowest energy triplet structure is predicted to lie more than 30 kcal/mol above the lowest energy singlet structure using the B3LYP* method. Thus triplet $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_4$ structures are not likely to be chemically significant.

The $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_4$ global minimum, **4S-1**, is a *cis* structure with two bridging CO groups and two terminal CO groups (Figure 2 and Table 1). Each $\eta^5\text{-C}_4\text{H}_4\text{P}$ ring is bonded to a single Fe atom as a pentahapto ligand similar to the cyclopentadienyl ligand. The Fe–Fe distance of 2.573 Å (B3LYP*) is similar to the experimental distance of

2.54 Å for the cyclopentadienyl analogue $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\mu\text{-CO})_2(\text{CO})_2$ and suggests a similar formal single bond. This gives each iron atom in **4S-1** the favored 18-electron configuration. The $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\mu\text{-CO})_2(\text{CO})_2$ structure **4S-2** (C_2), lying only 1.2 kcal/mol (B3LYP*) in energy above **4S-1**, differs from **4S-1** only in the relative orientation of the phosphorus atoms in the $\eta^5\text{-C}_4\text{H}_4\text{P}$ rings.

Figure 2. The eight lowest-energy singlet $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_4$ structures.

Table 1. Total energies (E , in hartree), relative energies (ΔE , in kcal/mol), and Fe-Fe distances (Å) for the $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_4$ structures. None of these structures has any imaginary vibrational frequencies.

	4S-1 (C_1 , 1A)	4S-2 (C_2 , 1A)	4S-3 (C_2 , 1A_g)	4S-4 (C_i , 1A_g)	4S-5 (C_1 , 1A)	4S-6 (C_1 , 1A)	4S-7 (C_i , 1A_g)	4S-8 (C_1 , 1A)
B3LYP*								
$-(E+3972)$	0.47734	0.47536	0.47326	0.47327	0.47194	0.47174	0.47021	0.46102
ΔE	0.0	1.2	2.6	2.6	3.4	3.5	4.5	10.2
Fe-Fe	2.573	2.568	2.574	2.770	2.757	2.759	2.749	3.871

The $(C_4H_4P)_2Fe_2(CO)_4$ structure **4S-3**, lying 2.6 kcal/mol (B3LYP*) in energy above **4S-1**, is a *trans* structure with two bridging CO groups, two terminal CO groups, and two terminal η^5 - C_4H_4P rings (Figure 2 and Table 1). The predicted Fe–Fe distance of 2.574 Å (B3LYP*) suggests a formal single bond thereby giving each iron atom the favored 18-electron configuration.

The $(C_4H_4P)_2Fe_2(CO)_4$ structures **4S-4** (C_i), **4S-5** (C_1), **4S-6** (C_1), and **4S-7** (C_i) are all low-energy unbridged structures lying within 5 kcal/mol of **4S-1** with each iron atom bearing two terminal CO groups (Figure 2 and Table 1). These structures differ in the relative orientation of their ring phosphorus atoms. The unbridged Fe–Fe distances in these structures of ~ 2.75 Å are significantly longer than the doubly bridged Fe–Fe distances in the $(C_4H_4P)_2Fe_2(CO)_4$ structures **4S-1**, **4S-2**, and **4S-3** but still suggest formal single bonds thereby giving each iron atom the favored 18-electron configuration.

The $(C_4H_4P)_2Fe_2(CO)_4$ structure **4S-8**, lying 10.2 kcal/mol (B3LYP*) in energy above **4S-1**, has two terminal CO groups bonded to each iron atom, two bridging C_4H_4P rings, and a non-bonding Fe $\cdots$ Fe distance of 3.871 Å (B3LYP*). One phospholyl ring is a η^5, η^1 -ligand bonded to one iron atom as a pentahapto ligand and to the other iron atom through a P $\rightarrow$ Fe dative bond of length 2.191 Å (B3LYP*), thus functioning as a seven-electron donor to the central Fe_2 unit. The other phospholyl ring is a η^4, η^1 -ligand bonded to one iron atom as a tetrahapto ligand and to the other iron atom through a normal P–Fe covalent bond of length 2.394 Å, thereby functioning as a five-electron donor ligand to the central Fe_2 unit. This combination of ligands and the lack of an iron-iron bond in **4S-8** give each iron atom the favored 18-electron configuration.

3.1.2. $(C_4H_4P)_2Fe_2(CO)_3$. Seven low energy $(C_4H_4P)_2Fe_2(CO)_3$ structures were found, namely one singlet and six triplets (Figure 3 and Table 2). The lowest energy $(C_4H_4P)_2Fe_2(CO)_3$ structure **3T-1** has a single bridging CO group, a terminal five-electron donor pentahapto η^5 - C_4H_4P ring, and a bridging seven-electron donor η^1, η^5 - C_4H_4P ring bonded as a pentahapto ligand to one iron atom and through a P $\rightarrow$ Fe dative bond to the other iron atom. The predicted Fe–Fe distance of 2.609 Å (B3LYP*), suggests the formal single bond required to give each iron atom the favored 18-electron configuration.

The $(C_4H_4P)_2Fe_2(CO)_3$ structure **3T-2**, lying only 1.0 kcal/mol (B3LYP*) in energy above **3T-1**, has three bridging CO groups and two η^5 - C_4H_4P rings and is closely related to the known cyclopentadienyl derivatives $(\eta^5-C_5R_5)_2Fe_2(\mu-CO)_3$ ($R = H, CH_3$) [5, 6, 7, 8]. The Fe=Fe distance of 2.270 Å (B3LYP*) in **3T-2** is very similar to the experimental Fe=Fe distance of 2.265 Å in $(\eta^5-Me_5C_5)_2Fe_2(\mu-CO)_3$ suggesting a similar formal double $\sigma + \frac{1}{2}\pi$ bond. This gives each iron atom in **3T-2** the favored 18-electron

configuration. The two unpaired electrons in the triplet spin state of **3T-2** reside in the formal double bond as two orthogonal π half-bonds similar to that suggested for the $(\eta^5\text{-R}_5\text{C}_5)_2\text{Fe}_2(\mu\text{-CO})_3$ derivatives. The $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_3$ structure **3T-3**, with C_{2v} symmetry, has almost the same total energy and geometrical configuration as **3T-2** except for the relative orientation of the ring phosphorus atoms..

Figure 3. The seven lowest-energy $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_3$ structures.

The $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_3$ structure **3T-4**, lying 5.2 kcal/mol (B3LYP*) in energy above **3T-1**, has one bridging CO group, two terminal CO groups, and terminal pentahapto $\eta^5\text{-C}_4\text{H}_4\text{P}$ rings (Figure 3 and Table 2). The Fe–Fe distance of 2.460 Å (B3LYP*) in **3T-4** suggests a formal single bond thereby giving each iron atom a 17-electron configuration for a binuclear triplet.

The $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_3$ structure **3T-5**, lying 5.5 kcal/mol in energy above **3T-1**, has two terminal pentahapto $\eta^5\text{-C}_4\text{H}_4\text{P}$ rings and three terminal CO groups (Figure 3 and Table 2). The Fe–Fe distance of 2.589 Å (B3LYP*) can be interpreted as a formal single bond. This gives each iron atom the 17-electron configuration for a binuclear triplet, provided that the iron atom bearing two CO groups has a formal positive charge and the iron atom bearing only one CO group has a formal negative charge.

Table 2. Total energies (E, in hartree), relative energies (ΔE , in kcal/mol), Fe-Fe distances (Å), numbers of the imaginary vibrational frequencies (Nimg), and spin contamination values ($\langle S^2 \rangle$) for the lowest energy $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_3$ structures.

	3T-1 (C ₁ , ³ A)	3T-2 (C ₂ , ³ B)	3T-3 (C _{2v} , ³ B ₁)	3T-4 (C ₂ , ³ B)	3T-5 (C ₁ , ³ A)	3T-6 (C ₁ , ³ A)	3S-1 (C ₁ , ¹ A)
B3LYP*							
–(E+3859)	0.15964	0.15809	0.15758	0.15142	0.15084	0.14843	0.14108
ΔE	0.0	1.0	1.3	5.2	5.5	7.0	11.6
Fe-Fe	2.609	2.270	2.267	2.460	2.589	2.564	2.447
Nimg	0	0	0	1	0	0	0
$\langle S^2 \rangle$	2.1	2.1	2.1	2.1	2.3	2.1	0.0

The $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_3$ structure **3T-6**, lying 7.0 kcal/mol (B3LYP*) in energy above **3T-1**, has a bridging CO group and a terminal CO group bonded to each iron atom. One of the phospholyl rings in **3T-6** is a terminal pentahapto $\eta^5\text{-C}_4\text{H}_4\text{P}$ ring whereas the other phospholyl ring is a seven-electron donor bridging $\eta^5, \eta^1\text{-C}_4\text{H}_4\text{P}$ ring bonded to one iron atom as a pentahapto ligand and to the other iron atom through a dative P→Fe bond of length 2.464 Å. The Fe-Fe distance of 2.564 Å (B3LYP*) suggests a formal single bond. The triplet spin state of **3T-6** can be rationalized by assigning the iron atom bonded to the terminal $\eta^5\text{-C}_4\text{H}_4\text{P}$ ring a 19-electron configuration and the other iron atom a 17-electron configuration.

The lowest energy singlet $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_3$ structure **3S-1**, lying 11.6 kcal/mol (B3LYP*) in energy above **3T-1**, has two bridging CO groups, one terminal CO group and two terminal pentahapto $\eta^5\text{-C}_4\text{H}_4\text{P}$ rings (Figure 3 and Table 2). The Fe=Fe distance in **3S-1** of 2.447 Å (B3LYP*) is ~0.13 Å shorter than that in the doubly CO-bridged $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ structures and thus suggests a formal Fe=Fe double bond in **3S-1**. Each iron atom in **3S-1** has the favored 18-electron configuration provided that the iron atom bearing the terminal CO group has a formal positive charge and the other iron atom has a corresponding negative charge.

3.1.3. $(C_4H_4P)_2Fe_2(CO)_2$. Six low-energy $(C_4H_4P)_2Fe_2(CO)_2$ structures (two singlets and four triplets) were found within 20 kcal/mol in energy using the B3LYP* method (Figure 4 and Table 3). The $(C_4H_4P)_2Fe_2(CO)_2$ global minimum **2T-1** has two terminal CO groups and two seven-electron donor bridging η^1, η^5 - C_4H_4P rings, bonded to one iron atom as a pentahapto ligand and to the other iron atom through a P→Fe dative bond of length ~ 2.37 Å. The Fe-Fe distance of 2.654 Å (B3LYP*) can correspond to a relatively long formal single bond. However, if this Fe-Fe distance is interpreted as a non-bonding distance forced to be relatively short because of the geometry of the bridging η^5, η^1 - C_4H_4P ligands, then each iron atom has a 17-electron configuration consistent with a binuclear triplet.

Figure 4. The six lowest energy $(C_4H_4P)_2Fe_2(CO)_2$ structures.

Table 3. Total energies (E , in hartree), relative energies (ΔE , in kcal/mol), and Fe-Fe distances (Å) for the six lowest energy $(C_4H_4P)_2Fe_2(CO)_2$ structures. None of these structures has any imaginary vibrational frequencies.

	2T-1 (C_1 , 3A)	2T-2 (C_1 , 3A)	2T-3 (C_1 , 3A)	2T-4 (C_1 , 3A)	2S-1 (C_{2v} , 1A_1)	2S-2 (C_s , $^1A'$)
B3LYP*						
-($E+3745$)	0.84339	0.84038	0.83823	0.83544	0.82777	0.82684
ΔE	0.0	1.9	3.2	5.0	9.8	10.4
Fe-Fe	2.654	2.4720	2.605	2.360	2.142	2.139
$\langle S^2 \rangle$	2.1	2.3	3.1	2.8	0.0	0.0

The $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_2$ structure **2T-2**, lying 1.9 kcal/mol in energy above **2T-1**, has two terminal CO groups bonded to the same iron atom (Figure 4 and Table 3). One phospholyl ring in **2T-2** is a terminal pentahapto $\eta^5\text{-C}_4\text{H}_4\text{P}$ ligand whereas the other phospholyl ring is a seven-electron donor bridging $\eta^5, \eta^1\text{-C}_4\text{H}_4\text{P}$ ligand. The Fe–Fe distance of 2.472 Å (B3LYP*) suggest a formal single bond. This gives the iron atom bearing two terminal CO groups the favored 18-electron configuration, whereas the other iron atom has only a 16-electron configuration. The $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_2$ structure **2T-3**, lying 3.2 kcal/mol in energy above **2T-1** is similar to **2T-2** except that the terminal CO groups are distributed evenly between the two iron atoms. This leads to a longer Fe–Fe single bond of 2.605 Å in **2T-3** relative to **2T-2**.

The $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_2$ structure **2T-4**, lying 5.0 kcal/mol in energy above **2T-1**, has two bridging CO groups and two terminal $\eta^5\text{-C}_4\text{H}_4\text{P}$ rings (Figure 4 and Table 3). The Fe=Fe distance of 2.360 Å (B3LYP*) can be interpreted as a formal double bond. This gives each iron atom the 17-electron configuration for a binuclear triplet.

The lowest energy singlet $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_2$ structure **2S-1**, lying 9.8 kcal/mol in energy above **2T-1**, is a C_{2v} structure with terminal pentahapto $\eta^5\text{-C}_4\text{H}_4\text{P}$ rings and bridging CO groups similar to **2T-4** (Figure 4 and Table 3). The Fe≡Fe distance of 2.142 Å (B3LYP*) in **2S-1** is ~0.2 Å shorter than that in **2T-4**. This suggests the formal triple bond required to give each iron atom the favored 18-electron configuration. The singlet $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_2$ structure **2S-2**, lying 10.4 kcal/mol in energy above **2T-1**, is similar to **2S-1** except for the orientation of the phosphorus atoms in the phospholyl rings.

3.2 Carbonyl rich structures

3.2.1 $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_6$. Two low-energy structures (one singlet and one triplet) were found for $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_6$ (Figure 5 and Table 4). The lower energy structure is the singlet **6S-1** with two bridging CO groups, four terminal CO groups, one pentahapto $\eta^5\text{-C}_4\text{H}_4\text{P}$ ring, and one monohapto $\eta^1\text{-C}_4\text{H}_4\text{P}$ ring. The monohapto $\eta^1\text{-C}_4\text{H}_4\text{P}$ ring is bonded to the iron atom bearing three terminal CO groups whereas the pentahapto $\eta^5\text{-C}_4\text{H}_4\text{P}$ ring is bonded to the iron atom bearing a single terminal CO group. The Fe–Fe distance of 2.638 Å (B3LYP*) in **6S-1** suggests a formal single Fe-Fe bond leading to the favored 18-electron configuration for each iron atom.

The triplet $(\text{C}_4\text{H}_4\text{P})_2\text{Fe}_2(\text{CO})_6$ structure **6T-1**, lying 4.3 kcal/mol (B3LYP*) in energy above **6S-1**, has six terminal CO groups equally distributed between two iron atoms (Figure 5 and Table 4). The bridging $\eta^1, \eta^1\text{-C}_4\text{H}_4\text{P}$ ring in **6T-1**, considered as a neutral ligand, donates a single electron to one iron atom and a pair of electrons (through the phosphorus lone pair) to the other iron atom. The $\eta^1\text{-C}_4\text{H}_4\text{P}$ ring is bonded to one of

the iron atoms and donates a single electron to that iron atom. The Fe–Fe distance of 2.665 Å (B3LYP*) suggests a formal single bond. This gives each iron atom in **6T-1** the 17-electron configuration for a binuclear triplet.

Figure 5. The singlet and triplet $(C_4H_4P)_2Fe_2(CO)_6$ structures.

Table 4. Total energies (E , in hartree), relative Energies (ΔE , in kcal/mol), Fe-Fe distances (Å), and spin contamination values $\langle S^2 \rangle$ for the two lowest energy $(C_4H_4P)_2Fe_2(CO)_6$ structures. Neither structure has any imaginary vibrational frequencies.

	6S-1 (C_1 , 1A)	6T-1 (C_s , 3A)
B3LYP*		
–($E+4199$)	0.04298	0.03606
ΔE	0.0	4.3
Fe-Fe	2.638	2.665
$\langle S^2 \rangle$	0.0	2.0

3.2.2. $(C_4H_4P)_2Fe_2(CO)_5$. Two low-lying $(C_4H_4P)_2Fe_2(CO)_5$ singlet structures were found (Figure 6, Table 5). The lower energy structure **5S-1** has two bridging CO groups, and three terminal CO groups. A terminal monohapto η^1 - C_4H_4P ring is bonded to the iron atom bearing two terminal CO groups with an unusually short Fe=P bond of 2.143 Å. On the basis of this short Fe=P distance, this phosphorus atom can be considered as a three-electron donor to the iron atom. A terminal pentahapto η^5 - C_4H_4P ring is bonded to the iron atom bearing only a single terminal CO group. The Fe–Fe distance of 2.592 Å (B3LYP*) suggests a formal single bond, thereby giving each iron atom the favored 18-electron configuration.

The $(C_4H_4P)_2Fe_2(CO)_5$ structure **5S-2**, lying 3.9 kcal/mol (B3LYP*) in energy above **5S-1**, has two bridging CO groups and three terminal CO groups (Figure 6 and Table 5). One of the phospholyl ligands is a terminal pentahapto η^5 - C_4H_4P ligand and is bonded to the iron atom bearing a single terminal CO group. The other phospholyl

ligand is an unusual terminal dihapto η^2 -C₄H₄P ligand that can function as a three-electron donor if considered formally as a neutral ligand. The Fe–Fe distance of 2.596 Å (B3LYP*) suggests a formal single bond, thereby giving each iron atom in **5S-2** the favored 18-electron configuration.

Figure 6. The two optimized (C₄H₄P)₂Fe₂(CO)₅ structures.

Table 5. Total energies (E , in hartree), relative energies (ΔE , in kcal/mol), and Fe-Fe distances (Å) for the two lowest energy (C₄H₄P)₂Fe₂(CO)₅ structures. Neither structure has any imaginary vibrational frequencies.

	5S-1 (C_1 , 1A)	5S-2 (C_1 , 1A)
B3LYP*		
-(E+4085)	0.73984	0.73360
DE	0.0	3.9
Fe-Fe	2.592	2.596

3.3. Thermochemistry.

Table 6 shows the dissociation energies for the reactions (C₄H₄P)₂Fe₂(CO) _{n} $\rightarrow$ (C₄H₄P)₂Fe₂(CO) _{$n-1$} + CO ($n = 6, 5, 4, 3$). The dissociation energy for the loss of one CO group from (C₄H₄P)₂Fe₂(CO)₅ is within ~4 kcal/mol of being thermoneutral suggesting a species that is not viable. However, the CO dissociation energies for the other (C₄H₄P)₂Fe₂(CO) _{n} species ($n = 6, 4, 3$) are all positive and greater than ~22 kcal/mol suggesting viability towards CO dissociation. In fact, these predicted CO dissociation energies for the (C₄H₄P)₂Fe₂(CO) _{n} derivatives ($n = 6, 4, 3$) are comparable to the experimental CO dissociation energies of 27, 41, and 37 kcal/mol for the stable metal carbonyls Ni(CO)₄, Fe(CO)₅, and Cr(CO)₆, respectively [41].

Table 6. Dissociation energies (kcal/mol) for the successive removal of carbonyl groups from the $(C_4H_4P)_2Fe_2(CO)_n$ derivatives

	B3LYP	BP86	B3LYP*
$(C_4H_4P)_2Fe_2(CO)_6(6S-1) \rightarrow (C_4H_4P)_2Fe_2(CO)_5(5S-1) + CO$	22.7	24.9	23.8
$(C_4H_4P)_2Fe_2(CO)_5(5S-1) \rightarrow (C_4H_4P)_2Fe_2(CO)_4(4S-1) + CO$	-3.8	1.5	-1.7
$(C_4H_4P)_2Fe_2(CO)_4(4S-1) \rightarrow (C_4H_4P)_2Fe_2(CO)_3(3S-1) + CO$	42.5	48.0	44.6
$(C_4H_4P)_2Fe_2(CO)_3(3T-1) \rightarrow (C_4H_4P)_2Fe_2(CO)_2(2T-1) + CO$	23.6	44.7	32.0
$(C_4H_4P)_2Fe_2(CO)_3(3S-1) \rightarrow (C_4H_4P)_2Fe_2(CO)_2(2S-1) + CO$	27.9	34.8	30.2

Table 7 lists the energies for the disproportionation reactions $2(C_4H_4P)_2Fe_2(CO)_n \rightarrow (C_4H_4P)_2Fe_2(CO)_{n+1} + (C_4H_4P)_2Fe_2(CO)_{n-1}$ ($n = 5, 4, 3$). This process is strongly endothermic for the tetracarbonyl $(C_4H_4P)_2Fe_2(CO)_4$ at ~46 kcal/mol indicating the tetracarbonyl to be a viable species. The disproportionations of the tricarbonyl and pentacarbonyl $(C_4H_4P)_2Fe_2(CO)_n$ ($n = 5, 3$) are exothermic suggesting that they are not viable species.

Table 7. Disproportionation Energies (kcal/mol) for the reactions $2(C_4H_4P)_2Fe_2(CO)_n \rightarrow (C_4H_4P)_2Fe_2(CO)_{n+1} + (C_4H_4P)_2Fe_2(CO)_{n-1}$

	B3LYP	BP86	B3LYP*
$2(C_4H_4P)_2Fe_2(CO)_5(5S-1) \rightarrow (C_4H_4P)_2Fe_2(CO)_4(4S-1) + (C_4H_4P)_2Fe_2(CO)_6(6S-1)$	-26.5	-23.4	-25.5
$2(C_4H_4P)_2Fe_2(CO)_4(4S-1) \rightarrow (C_4H_4P)_2Fe_2(CO)_3(3S-1) + (C_4H_4P)_2Fe_2(CO)_5(5S-1)$	46.3	46.4	46.3
$2(C_4H_4P)_2Fe_2(CO)_3(3S-1) \rightarrow (C_4H_4P)_2Fe_2(CO)_2(2S-1) + (C_4H_4P)_2Fe_2(CO)_4(4S-1)$	-14.6	-13.2	-14.4
$2(C_4H_4P)_2Fe_2(CO)_3(3T-1) \rightarrow (C_4H_4P)_2Fe_2(CO)_2(2T-1) + (C_4H_4P)_2Fe_2(CO)_4(4S-1)$	-7.8	5.4	-0.9

Also of interest is the dissociation of the $(C_4H_4P)_2Fe_2(CO)_n$ derivatives into mononuclear $(C_4H_4P)Fe(CO)_m$ fragments. In order to obtain such energetic data, the structures of the mononuclear $(C_4H_4P)Fe(CO)_m$ were optimized by the same DFT methods as used to study the binuclear derivatives (Figure 7). Using this information, the dissociation energies of the binuclear $(C_4H_4P)_2Fe_2(CO)_n$ into mononuclear fragments were determined (Table 8). The results were found to depend on the density functional used since the mononuclear $(C_4H_4P)Fe(CO)_n$ are necessarily doublet spin state structures and energy differences between different spin state isomers are dependent on the density functional used. However, dissociation of the pentacarbonyl $(C_4H_4P)_2Fe_2(CO)_5$ into the mononuclear fragments $(C_4H_4P)Fe(CO)_3$ and $(C_4H_4P)Fe(CO)_2$ appears to be either slightly exothermic (B3LYP) or nearly thermoneutral (B3LYP*) by two of the DFT

methods and the least endothermic (16.9 kcal/mol) by the BP86 method. The other $(C_4H_4P)_2Fe_2(CO)_n$ ($n = 6, 4, 3, 2$) appear to be viable with respect to dissociation into mononuclear fragments with the dissociation energies increasing with decreasing numbers of CO groups similar to related systems.

Figure 7. The optimized geometries for the mononuclear structures $(C_4H_4P)Fe(CO)_m$ ($m = 3, 2, 1$).

Table 8. Dissociation energies of the binuclear $(C_4H_4P)_2Fe_2(CO)_n$ ($n = 5, 4, 3, 2$) into mononuclear fragments (kcal/mol)

	B3LYP	BP86	B3LYP*
$(C_4H_4P)_2Fe_2(CO)_6$ (6S-1) $\rightarrow$ $2(C_4H_4P)Fe(CO)_3$	7.0	23.1	12.5
$(C_4H_4P)_2Fe_2(CO)_5$ (5S-1) $\rightarrow$ $(C_4H_4P)Fe(CO)_2 + (C_4H_4P)Fe(CO)_3$	-6.0	16.9	1.2
$(C_4H_4P)_2Fe_2(CO)_4$ (4S-1) $\rightarrow$ $2(C_4H_4P)Fe(CO)_2$	7.5	34.0	15.3
$(C_4H_4P)_2Fe_2(CO)_3$ (3T-1) $\rightarrow$ $(C_4H_4P)Fe(CO)_2 + (C_4H_4P)Fe(CO)$	29.7	57.0	39.2
$(C_4H_4P)_2Fe_2(CO)_2$ (2S-1) $\rightarrow$ $2(C_4H_4P)Fe(CO)$	44.4	75.7	54.3

3.4 NBO Analysis of the Iron-Iron Bonding

Table 9 lists the atomic natural charges for the iron atoms and the Wiberg Bond Indices (WBI) for the Fe-Fe bonds using NBO analysis with the B3LYP* functional [42]. The Fe-Fe distances, the formal Fe-Fe bond orders, and the bridging groups are also listed for comparison. Only the singlet structures are considered since WBI analyses of higher spin state structures appear to be less reliable.

Previous studies on the Wiberg Bond Indices (WBIs) of metal carbonyls such as $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ show that the WBI values are relatively low compared with the formal bond orders, particularly when the metal-metal bonds are bridged by carbonyl groups [43]. This is also true for the $(C_4H_4P)_2Fe_2(CO)_n$ derivatives, with no WBI values greater than 0.6. However, the relative WBIs of the iron-iron bonds still correlate well with the formal bond orders suggested by Fe-Fe distances and electron counting.

The WBI values for the Fe-Fe bonds in the $(C_4H_4P)_2Fe_2(CO)_n$ derivatives depend on the formal bond order and the number of bridging groups (Table 9). Increasing the number of bridging groups generally lowers the WBI values, presumably because of

multicenter bonding involving the bridging group and the iron atoms. Most of the structures reported in this paper have two bridging CO groups with WBI values for formal Fe-Fe single bonds ranging from 0.13 to 0.20. The formal Fe=Fe double bond in **3S-2** and the formal Fe≡Fe triple bonds in **2S-1** and **2S-2**, all with two CO bridges, have correspondingly higher WBIs of 0.28 and 0.67, respectively. The unbridged Fe-Fe single bonds in the $(C_4H_4P)_2Fe_2(CO)_4$ structures have higher WBIs than doubly CO-bridged Fe-Fe single bonds, ranging from 0.30 to 0.32. The relatively high energy $(C_4H_4P)_2Fe_2(CO)_4$ structure **4S-8** having two bridging phospholyl ligands and a long non-bonding Fe...Fe distance of 3.871 Å has a nearly zero WBI of 0.02.

Table 9. Atomic charges and Wiberg bond indices for the singlet $(C_4H_4P)_2Fe_2(CO)_n$ structures by the BP86 method.

	Natural Charge on Fe / Fe	Wiberg bond index	Fe-Fe distance, Å	Bridges	Bond order
6S-1	-0.24/-0.54	0.13	2.638	2CO	1
5S-1	-0.32/-0.24	0.15	2.592	2CO	1
5S-2	-0.25/-0.34	0.19	2.596	2CO	1
4S-1	-0.24/-0.23	0.20	2.573	2CO	1
4S-2	-0.23/-0.23	0.20	2.568	2CO	1
4S-3	-0.22/-0.22	0.20	2.574	2CO	1
4S-4	-0.25/-0.25	0.30	2.770	none	1
4S-5	-0.24/-0.24	0.32	2.757	none	1
4S-6	-0.24/-0.24	0.32	2.759	none	1
4S-7	-0.23/-0.23	0.34	2.749	none	1
4S-8	-0.39/-0.36	0.02	3.871	2C ₄ H ₄ P	0
3S-1	0.11/-0.27	0.28	2.447	2CO	2
2S-1	-0.02/-0.02	0.67	2.142	2CO	3
2S-2	-0.01/-0.02	0.67	2.139	2CO	3

5. Summary

The low-energy $(C_4H_4P)_2Fe_2(CO)_n$ ($n = 4, 3, 2$) structures have direct iron-iron bonds and terminal five-electron donor pentahapto η^5 -C₄H₄P rings with the phosphorus lone pairs not involved in the bonding to the iron atoms. They are thus analogous to the corresponding cyclopentadienyl derivatives. However, they differ from the binuclear phospholyl manganese carbonyls $(C_4H_4P)_2Mn_2(CO)_n$ ($n = 5, 4$), for which structures with bridging seven-electron donor η^5, η^1 -C₄H₄P phospholyl rings using the phosphorus lone pairs as well as the ring π -electrons for ligand-manganese bonding are greatly favored energetically.

Partially bonded phospholyl rings, as well as direct Fe-Fe bonds, are found in the carbonyl-rich $(C_4H_4P)_2Fe_2(CO)_n$ ($n = 6, 5$) species. The pentacarbonyl $(C_4H_4P)_2Fe_2(CO)_5$ does not appear to be a viable species since loss of CO to give $(C_4H_4P)_2Fe_2(CO)_4$ is essentially thermoneutral and disproportionation into $(C_4H_4P)_2Fe_2(CO)_6 + (C_4H_4P)_2Fe_2(CO)_4$ is significantly exothermic at ~ 25 kcal/mol.

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Literature References

- [1] T. S. Piper, G. Wilkinson, *J. Inorg. Nucl. Chem.*, 6 (1956) 104.
- [2] O. S. Mills, *Acta Cryst.* 11 (1958) 620.
- [3] R. F. Bryan, P. T. Greene, *J. Chem. Soc., A*, (1970) 3068.
- [4] A. Mitschler, B. Rees, M. S. Lehmann, *J. Am. Chem. Soc.* 100 (1978) 3390.
- [5] J. V. Caspar, T. J. Meyer, *J. Am. Chem. Soc.* 102 (1980) 7794.
- [6] R. H. Hooker, K. A. Mahmoud, A. J. Rest, *Chem. Commun.* (1983) 1022.
- [7] A. F. Hepp, J. P. Blaha, C. Lewis, M. S. Wrighton, *M. S. Organometallics* 3 (1984) 174.
- [8] J. P. Blaha, B. E. Bursten, J. C. Dewan, R. B. Frankel, C. L. Randolph, B. A. Wilson, M. S. Wrighton, *J. Am. Chem. Soc.* 107 (1985) 4561.
- [9] R. B. King, *Inorg. Chem.* 5 (1966) 2227.

- [10] H. Wang, Y. Xie, R. B. King, H. F. Schaefer, *Inorg. Chem.*, 45 (2006) 3384.
- [11] K.B. Dillon, F. Mathey, J.F. Nixon, *Phosphorus: The Carbon Copy: From Organophosphorus to Phospha-organic Chemistry*, Wiley VCH, New York, 1998.
- [12] F. Mathey, *Tetrahedron Lett.* (1976) 4155.
- [13] F. Mathey, A. Mitschler, R. Weiss, *J. Am. Chem. Soc.* 100 (1978) 5748.
- [14] X. Chen, Q. Du, R. Jin, H. Feng, Y. Xie, R. B. King, *New J. Chem.*, 35 (2011) 1117.
- [15] I. Bernal, J. D. Korp, W. A. Hermann, R. Serrano, *Chem. Ber.* 117 (1984) 434.
- [16] X. Chen, R. Jin, Q. Du, H. Feng, Y. Xie, R. B. King, *J. Organometal. Chem.*, 701 (2012) 1.
- [17] A. A. Bengali, R. G. Bergman, C. B. Moore, *J. Am. Chem. Soc.* 117 (1995) 3879.
- [18] W.I. Bailey, D.M. Collins, F.A. Cotton, J.C. Baldwin, *J. Organometal. Chem.* 165 (1979) 373.
- [19] H. Wang, Y. Xie, R.B. King, H.F. Schaefer, *J. Am. Chem. Soc.* 127 (2005) 11646.
- [20] T. Ziegler, J. Autschbach, *Chem. Rev.*, 105 (2005) 2695.
- [21] M. Bühl, H. Kabrede, *J. Chem. Theory Comput.*, 2 (2006) 1282.
- [22] M. Brynda, L. Gagliardi, P. O. Widmark, P. P. Power, B. O. Roos, *Angew. Chem. Int. Ed.*, 45 (2006) 3804.
- [23] N. Sieffert, M. Bühl, *J. Am. Chem. Soc.*, 132 (2010) 8056.
- [24] P. Schyman, W. Lai, H. Chen, Y. Wang, S. Shaik, *J. Am. Chem. Soc.*, 133 (2011) 7977.
- [25] R. D. Adams, W. C. Pearl, Y.O. Wong, Q. Zhang, M. B. Hall, J. R. Walensky, *J. Am. Chem. Soc.*, 133 (2011) 12994.
- [26] R. Lonsdale, J. Olah, A. J. Mulholland, J. N. Harvey, *J. Am. Chem. Soc.*, 133 (2011) 15464.
- [27] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [28] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [29] A.D. Becke, *Phys. Rev.* 38 (1988) 3098.
- [30] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B.* 37 (1988) 785.
- [31] M. Reiher, O. Salomon, B. A. Hess, *Theor. Chem. Acc.* 107 (2001) 48.
- [32] O. Salomon, M. Reiher, B. A. Hess, *J. Chem. Phys.* 117 (2002) 4729.
- [33] V. Jones, W. Thiel, *J. Phys. Chem.*, 102 (1995) 8474.
- [34] I. Silaghi-Dumitrescu, T. E. Bitterwolf, R. B. King, *J. Am. Chem. Soc.*, 128 (2006) 5432.
- [35] T. H. Dunning, *J. Chem. Phys.* 53 (1970) 2823.

- [36] S. Huzinaga, J. Chem. Phys., 42 (1965) 1293.
- [37] A. J. H. Wachters, J. Chem. Phys. 52 (1970) 1033.
- [38] D. M. Hood, R. M. Pitzer, H. F. Schaefer, J. Chem. Phys. 71 (1979) 705.
- [39] M. J. Frisch, et al. Gaussian, Inc., Wallingford CT, 2009. Gaussian 09, Revision A.02.
- [40] B. N. Papas, H. F. Schaefer, J. Mol. Struct. (THEOCHEM) 768 (2006) 175.
- [41] L. S. Sunderlin, D. Wang, P. R. Squires, J. Am. Chem. Soc., 115(1993) 12060.
- [42] F. Weinhold, C. R. Landis, *Valency and Bonding: A Natural Bond Order Donor-Acceptor Perspective*, Cambridge University Press, Cambridge, England, U. K., 2005, pp. 32–36.
- [43] H. Wang, Y. Xie, R. B. King, H. F. Schaefer, J. Am. Chem. Soc. 128 (2006) 11376.

Graphical abstract