Binuclear phospholyl iron carbonyls: The limited role of the phosphorus atom in metal complexation

Xiaohong Chen [a], Li Yuan [a], Guiming Ren [a], Qiao Xi [a], Rong Jin [a], Quan Du [a], Hao Feng [a,*], Yaoming Xie [b], R. Bruce King [b,*]

[a] School of Physics and Chemistry, Research Center for Advanced Computation, Xihua University, Chengdu 610039, China
[b] Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, GA 30602, USA

ABSTRACT

The structures and thermodynamics of the binuclear phospholyl iron 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 $(C_4H_4P)_2Fe_2(CO)_6 + (C_4H_4P)_2Fe_2(CO)_4$.

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1. Introduction

The chemistry of cyclopentadienyliron carbonyls dates back 60 years to the synthesis of $(\eta^5$-$C_5H_5)_2Fe_2(CO)_2(\mu$-$CO)_2$ by Piper and Wilkinson in 1956 from the thermal reaction of $Fe(CO)_5$ with cyclopentadiene dimer at $\sim$130 °C [1]. Subsequently both *cis* and *trans* stereoisomers of $(\eta^5$-$C_5H_5)_2Fe_2(CO)_2(\mu$-$CO)_2$ were separated and structurally characterized by X-ray crystallography [2–4].
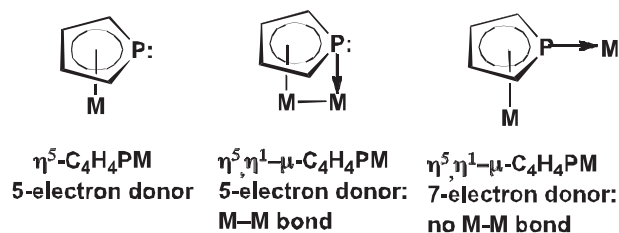
Interesting species have been obtained by decarbonylation of $(\eta^5$-$C_5H_5)_2Fe_2(CO)_2(\mu$-$CO)_2$. Photolysis under mild conditions gives the unsaturated $(\eta^5$-$C_5H_5)_2Fe_2(\mu$-$CO)_3$ [5–7], which is of interest as a stable triplet spin state metal carbonyl derivative. X-ray crystallography of the permethylated derivative $(\eta^5$-$Me_5C_5)_2Fe_2(\mu$-$CO)_3$ indicates a short Fe=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 $(\eta^5$-$C_5H_5)_2Fe_2(CO)_2(\mu$-$CO)_2$ by prolonged pyrolysis at $\sim$100 °C leads to the tetranuclear cluster $(\eta^5$-$C_5H_5)_4Fe_4(\mu_3$-$CO)_4$ containing a central Fe_4 tetrahedron with each face capped by a carbonyl group [9]. Theoretical studies on $(\eta^5$-$C_5H_5)_2Fe_2(CO)_n$ ($n = 4$, 3, 2) derivatives [10] suggest the formation of this cluster by dimerization of an

unsaturated doubly bridged $(\eta^5$-$C_5H_5)_2Fe_2(\mu$-$CO)_2$ with a short Fe≡Fe distance of $\sim$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, η^5-C_4H_4P, an analogue of the cyclopentadienyl ligand. Because of synthetic challenges, development of phospholyl-metal chemistry lagged considerably behind the development of cyclopentadienyl-metal chemistry. However, Mathey and coworkers [12,13] used the thermal reaction of P-phenyl-phosphole with $Mn_2(CO)_{10}$ to synthesize phospholyl manganese tricarbonyl $(\eta^4$-$C_4H_4P)Mn(CO)_3$. Comparison of the properties of $(\eta^5$-$C_4H_4P)Mn(CO)_3$ and $(\eta^5$-$C_5H_5)Mn(CO)_3$ 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 $(\eta^5$-$C_4H_4P)Mn(CO)_3$ 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 (Fig. 1). This possibility of a phospholyl ligand acting as a seven-electron donor bridge across

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* Corresponding authors.
  E-mail addresses: Fenghao@mail.xhu.edu.cn (H. Feng), rbking@chem.uga.edu (R. Bruce King).

η^5-C$_4$H$_4$PM
5-electron donor

η^5,η^1-μ-C$_4$H$_4$PM
5-electron donor:
M—M bond

η^5,η^1-μ-C$_4$H$_4$PM
7-electron donor:
no M-M bond

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

an M$_2$ unit suggested that binuclear phospholyl metal carbonyls might have significantly different chemistry than the corresponding cyclopentadienyl metal carbonyls.

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

The binuclear phospholyl cobalt carbonyls were found to be very different from the phospholyl manganese carbonyls in not having seven-electron donor bridging η^1,η^5-C$_4$H$_4$P rings in their energetically favored structures [16]. Thus the lowest energy (C$_4$H$_4$P)$_2$Co$_2$(CO)$_n$ (n = 3, 2, 1) structures were all found to have five-electron donor terminal η^5-C$_4$H$_4$P rings rather than seven-electron donor bridging η^5,η^1-phospholyl rings. In fact these lowest energy (C$_4$H$_4$P)$_2$Co$_2$(CO)$_n$ (n = 3, 2, 1) structures were found to be completely analogous to the isoelectronic phosphorus-free structures (C$_5$H$_5$)$_2$Co$_2$(CO)$_n$ (n = 3, 2, 1), which have been synthesized [17,18] and studied by density functional theory [19]. In addition, higher energy (C$_4$H$_4$P)$_2$Co$_2$(CO)$_n$ (n = 3, 2, 1) structures were found in which the phospholyl ligand acts as a five-electron donor η^5,η^1-C$_4$H$_4$P ligand across a Co–Co bond (Fig. 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 (C$_4$H$_4$P)$_2$Fe$_2$(CO)$_n$ (n = 4, 3, 2) derivatives with their extensively studied cyclopentadienyl derivatives (C$_5$H$_5$)$_2$Fe$_2$(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)$_4$I$_2$ to give a phospholyl iron carbonyl iodide such as the unsubstituted (C$_4$H$_4$P)Fe(CO)$_2$I. Reductive deiodination of such species could then provide the binuclear (C$_4$H$_4$P)$_2$Fe$_2$(CO)$_4$ analogous to (η^5-C$_5$H$_5$)$_2$Fe$_2$(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 [20–26]. 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 (C$_4$H$_4$P)$_2$Fe$_2$(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 [30] 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 [31]. 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 v(CO) vibrational frequencies, the B3LYP method usually predicts higher values than the BP86 method by ~100 cm^{-1}. Previous work shows that the BP86 results are closer to the experimental v(CO) values without using any scaling factors [32,33]. 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 α_d(C) = 0.75 and α_d(O) = 0.85 to the standard Huzinaga–Dunning contracted DZ sets [34,35] and are designated (9s5p1d/4s2p1d). The DZP basis set used for phosphorus adds one set of pure spherical harmonic d functions with orbital exponents α_d(P) = 0.60 to the standard Huzinaga–Dunning contracted DZ sets and are designated (12s8p1d/6s4p1d). For hydrogen, a set of p polarization functions α_p(H) = 0.75 is added to the Huzinaga–Dunning DZ set. The loosely contracted DZP basis set for iron is the Wachters primitive set [36] augmented by two sets of p functions and a set of d functions, contracted following Hood, Pitzer, and Schaefer [37], 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 [38], exercising the fine grid option (75 radial shells, 302 angular points) for evaluating integrals numerically [39].

3. Results and discussion

3.1. Molecular structures

3.1.1. (C$_4$H$_4$P)$_2$Fe$_2$(CO)$_4$

Eight low-energy structures were found for (C$_4$H$_4$P)$_2$Fe$_2$(CO)$_4$; all of these structures are singlets (Fig. 2). Triplet (C$_4$H$_4$P)$_2$Fe$_2$(CO)$_4$ structures were also found. However, they are not discussed in this paper since the lowest energy triplet structure is predicted to lie