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Versatile Behavior of the Fluorophosphinidene Ligand in Iron Carbonyl Chemistry

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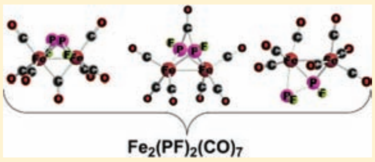
Ⓢ *Supporting Information*

ABSTRACT: Fluorophosphinidene (PF) is a versatile ligand found experimentally in the transient species $M(CO)_5(PF)$ (M = Cr, Mo) as well as the stable cluster $Ru_5(CO)_{15}(\mu_4\text{-}PF)$. The PF ligand can function as either a bent two-electron donor or a linear four-electron donor with the former being more common. The mononuclear tetracarbonyl $Fe(PF)(CO)_4$ is predicted to have a trigonal bipyramidal structure analogous to $Fe(CO)_5$ but with a bent PF ligand replacing one of the equatorial CO groups. The tricarbonyl $Fe(PF)(CO)_3$ is predicted to have two low-energy singlet structures, namely, one with a bent PF ligand and a 16-electron iron configuration and the other with a linear PF ligand and the favored 18-electron iron configuration. Low-energy structures of the dicarbonyl $Fe(PF)(CO)_2$ have bent PF ligands and triplet spin multiplicities. The lowest energy structures of the binuclear $Fe_2(PF)(CO)_8$ and $Fe_2(PF)_2(CO)_7$ derivatives are triply bridged structures analogous to the experimental structure of the analogous $Fe_2(CO)_9$. The three bridges in each $Fe_2(PF)(CO)_8$ and $Fe_2(PF)_2(CO)_7$ structure include all of the PF ligands. Other types of low-energy $Fe_2(PF)_2(CO)_7$ structures include the phosphorus-bridging carbonyl structure $(FP)_2COFe_2(CO)_6$, lying only ~2 kcal/mol above the global minimum, as well as an $Fe_2(CO)_7(\mu\text{-}P_2F_2)$ structure in which the two PF groups have coupled to form a difluorodiphosphene ligand unsymmetrically bridging the central Fe_2 unit.



1. INTRODUCTION

Simple two-atom ligands such as CO,[1] NO,[2,3] CN,[4−6] and N_2[7,8] containing only first row elements have historically played important roles in the development of transition metal coordination chemistry. In recent years the development of the chemistry of the CS ligand has extended the chemistry of simple two-atom ligands to second row elements.[9] Even more recently, the first metal complexes of the two-atom boron ligands BF[10] and BO[11] as well as the CF ligand[12] have been synthesized and characterized structurally.

Among these simple two-atom ligands the neutral NO ligand exhibits a novel duality in functioning as either a linear three-electron donor ligand or a bent one-electron donor ligand (Figure 1).[2,3] In the latter case the bent ligand geometry results in a stereochemically active lone pair. However, in the former case this lone pair is involved in the metal−ligand bond leading to the linear geometry. Adding one-electron to the NO ligand gives the hypothetical NF ligand. However, the anticipated strong fluorinating ability of such a ligand makes it incompatible with the low transition metal formal oxidation states typically involved in complexes.

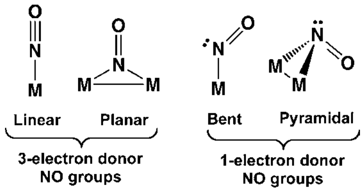


Figure 1. Three-electron and one-electron donor NO groups.

The fluorophosphinidene ligand (PF) is valence isoelectronic with the NF ligand but, unlike NF, is anticipated to be compatible with low transition metal oxidation states. In principle, the PF ligand could either be a bent two-electron donor ligand with a stereochemically active nonbonding lone pair or a linear four-electron donor ligand in which this lone pair is involved in the metal−ligand bonding (Figure 2). Free PF has been generated in molecular beams,[13] but is far too unstable to use as a reagent for the synthesis of metal complexes. However, the synthesis of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CF)$ by the defluorination of $(\eta^5\text{-}C_5H_5)Mo(CO)_3CF_3$ with potassium/graphite[12] suggests that similar defluorination of metal trifluorophosphine complexes might provide routes to

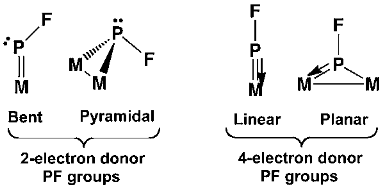


Figure 2. Two-electron and four-electron donor PF groups.

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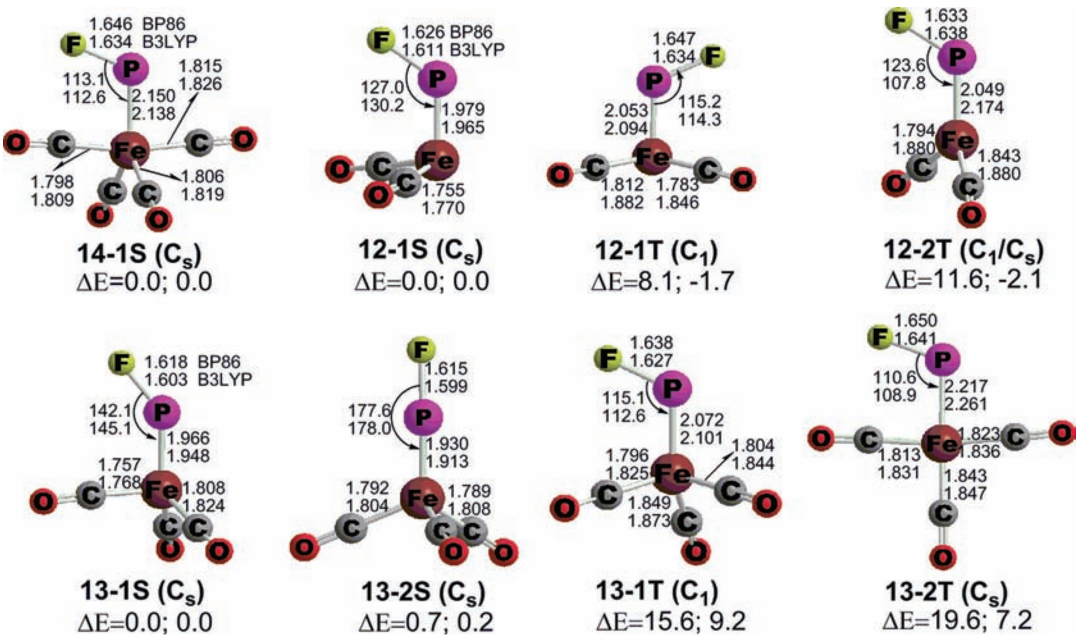


Figure 3. Optimized structures of the mononuclear Fe(PF)$(CO)_n$ (n = 4, 3, 2) derivatives.

Table 1. Relative Energies (Δ*E*, in kcal/mol), the Fe−Fe Bond Distances (in Å), and the Angles of the P−F Bond of Bridging PF Groups out of the Fe−P−Fe Plane (*θ*, in degrees) for the Optimized Structures of the $Fe_2(PF)(CO)_8$ and $Fe_2(PF)_2(CO)_7$ Complexes at the BP86/DZP and B3LYP/DZP Levels

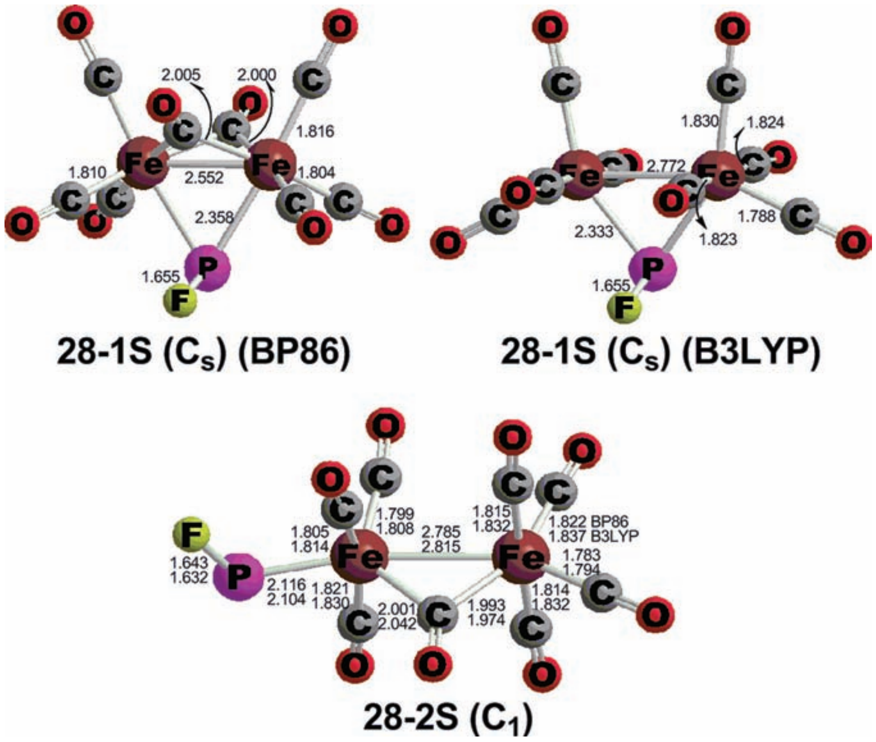
	BP86/DZP				B3LYP/DZP			
struct.	state (sym.)	Δ*E*	Fe−Fe	*θ* (deg)	state (sym.)	Δ*E*	Fe−Fe	*θ* (deg)
28−1S	C_s ($^1A'$)	0.0	2.552	71.2	C_s ($^1A'$)	0.0	2.772	69.9
28−2S	C_1 (^1A)	24.9	2.785		C_{2v} ($^1A_1$)	25.9	2.815	
27−1S	C_{2v} ($^1A_1$)	0.0	2.571	71.2	C_{2v} ($^1A_1$)	0.0	2.584	72.2
27−2S	C_{2v} ($^1A_1$)	2.4	2.671	32.2	C_{2v} ($^1A_1$)	2.0	2.668	30.9
27−3S	C_{2v} ($^1A_1$)	3.8	2.577	68.7	C_{2v} ($^1A_1$)	5.3	2.580	69.4
27−4S	C_1 (^1A)	6.3	2.826	39.0	C_1 (^1A)	0.6	2.862	37.1
27−5S	C_1 (^1A)	10.7	3.761	5.8(up)/69.4(down)	C_1 (^1A)	6.2	3.749	4.5(up)/70.6(down)
27−6S	C_1 (^1A)	15.5	2.715	68.7(up)/69.8(down)	C_1 (^1A)	12.7	2.754	69.5(up)/70.9(down)
27−7S	C_1 (^1A)	15.5	2.718	68.7(up)/69.4(down)	C_1 (^1A)	12.8	2.756	69.7(up)/70.6(down)
27−8S	C_1 (^1A)	19.2	4.063	7.7	C_1 (^1A)	15.8	4.065	7.7

metal fluorophosphinidene complexes. In addition, the species $M(CO)_5(PF)$ (M = Cr, Mo) with terminal fluorophosphinidene ligands have been generated by the pyrolysis of 7-fluoro-7-phosphanorbornadiene metal pentacarbonyl complexes, but these derivatives are unstable under the conditions where they are generated.[14] Metal clusters with bridging PF ligands are more stable as exemplified by the stable $Ru_5(CO)_{15}(\mu_4\text{-PF})$, which has been characterized structurally.[15] In recent years, metal complexes of other types of phosphinidene derivatives (RP and particularly R_2NP) have been studied.[16]

The research discussed in the current paper explores possible structures for the mononuclear Fe(PF)$(CO)_n$ (n = 4, 3, 2) and binuclear $Fe_2(PF)(CO)_8$ and $Fe_2(PF)_2(CO)_7$ using density functional theory (DFT). For the mononuclear derivatives the 18-electron rule suggests $Fe(PF)(CO)_4$ with a bent two-electron donor PF group analogous to $Fe(CO)_5$ and $Fe(PF)(CO)_3$ with a linear four-electron donor PF group as stable compounds. The binuclear derivatives $Fe_2(PF)(CO)_8$ and $Fe_2(PF)_2(CO)_7$ represent analogues of the well-known[17] $Fe_2(CO)_9$. However, in addition to $Fe_2(PF)_2(CO)_7$ structures analogous to the experimental $Fe_2(CO)_9$ structure, two other interesting low-energy structures were found for $Fe_2(PF)_2(CO)_7$, namely, a structure $(FP)_2COFe_2(CO)_6$ in which a CO group has inserted between the two PF groups and a structure $Fe_2(CO)_7(\mu\text{-}P_2F_2)$ in which the two PF ligands have coupled to form a difluorodiphosphene ligand, FP═PF.

2. THEORETICAL METHODS

DFT methods have been acknowledged to be a practical and effective computational tool, especially for organometallic compounds.[18−33] Two DFT approaches were employed herein, namely, the BP86 and B3LYP methods. The BP86 method is a pure DFT method combining Becke's 1988 exchange functional (B)[34] with Perdew's 1986 gradient correlation functional (P86)[35] whereas the B3LYP method is an HF/DFT hybrid method using Becke's three-parameter functional (B3)[36] and the Lee−Yang−Parr generalized gradient correlation functional (LYP).[37] All-electron double-ζ plus polarization (DZP) basis sets were used. For C, O, F, and P atoms, the DZP basis sets begin with Huzinaga−Dunning−Hay[38−40] contracted double-ζ Gaussian basis sets and then add a set of pure spherical harmonic d-like polarization functions with orbital exponents $\alpha_d(C) = 0.75$, $\alpha_d(O) = 0.85$, $\alpha_d(F) = 1.0$, and $\alpha_d(P) = 0.6$. The contraction scheme is (9s5p1d/4s2p1d) for the C, O, and F atoms and (11s7p1d/6s4p1d) for the P atom. For Fe, the DZP basis set, designated as (14s11p6d/10s8p3d), uses the Wachters' primitive set[41] augmented by two sets of p functions and



28-1S (C_s) (BP86)

28-1S (C_s) (B3LYP)

28-2S (C_1)

Figure 4. Three optimized $Fe_2(PF)(CO)_8$ structures.

one set of d functions and is contracted following Hood et al.[42] For $Fe_2(PF)(CO)_8$ and $Fe_2(PF)_2(CO)_7$, there are 376 and 384 contracted Gaussian functions, respectively, with the present DZP basis sets.

All of the computations were carried out with the Gaussian 03 program.[43] Thus various structures of $Fe_2(PF)(CO)_8$, $Fe_2(PF)_2(CO)_7$, and $Fe(PF)(CO)_n$ (n = 4, 3, 2) were fully optimized using both the BP86 and the B3LYP methods. Harmonic vibrational frequencies were also calculated at the same levels by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The default integration grid (75, 302) of Gaussian 03 was used for evaluating integrals numerically, and the tight designation was employed for self-consistent field (SCF) convergence.

The geometries arising from the BP86/DZP and B3LYP/DZP optimizations are depicted in Figures 3 to 5 with all bond distances given in angstroms. Table 1 lists their electronic states and energies.

3. RESULTS AND DISCUSSION

3.1. Mononuclear Derivatives.

3.1.1. Fe(PF)(CO)$_4$. Only one low-energy structure, namely, the C_s singlet structure **14−1S** (Figure 3), was optimized for $Fe(PF)(CO)_4$ using either the BP86 or B3LYP method. This structure has trigonal bipyramidal geometry similar to the well-established structure for $Fe(CO)_5$. A bent two-electron donor PF ligand with an Fe−P−F angle of ~113° is located in an equatorial position of **14−1S** thereby giving the iron atom the favored 18-electron configuration.

3.1.2. Fe(PF)(CO)$_3$. Four $Fe(PF)(CO)_3$ structures were found, namely the two singlets **13−1S** and **13−2S** and the two triplets **13−1T** and **13−2T** (Figure 3). Structures **13−1S**, **13−2S**, and **13−1T** have tetrahedral or distorted tetrahedral iron coordination whereas structure **13−2T** has square planar iron coordination. The $Fe(PF)(CO)_3$ global minimum predicted by both BP86 and B3LYP methods is the C_s singlet structure **13−1S**. However, the singlet structure **13−2S** lies only 0.7 kcal/mol (BP86) or 0.2 kcal/mol (B3LYP) above **13−1S** so that these two structures are essentially degenerate. The $Fe(PF)(CO)_3$ structure **13−1S** can be derived from the $Fe(PF)(CO)_4$ structure **14−1S** by removal of the axial CO group, namely, the CO group trans to the PF ligand. The PF group in **13−1S** remains a two-electron donor bent ligand with an F−P−Fe angle of ~144°, so that the iron atom has only a 16-electron configuration. However, the PF ligand in **13−2S** has linear geometry and thus is a four-electron donor, thereby giving the iron atom the favored 18-electron configuration.

The two triplet $Fe(PF)(CO)_3$ structures are significantly higher energy structures lying 15.6 and 19.6 kcal/mol (BP86) or 9.2 and 7.2 kcal/mol (B3LYP) in energy, respectively, above the **13−1S** global minimum (Figure 3). Both **13−1T** and **13−2T** have two-electron donor bent PF ligands leading to 16-electron configurations for the iron atoms, consistent with the triplet spin states. Structures **13−1T** and**13−2T** differ in the iron coordination geometries, which are approximately tetrahedral and square planar, respectively.

3.1.3. Fe(PF)(CO)$_2$. Three structures are found for $Fe(PF)(CO)_2$, namely, one singlet and two triplets (Figure 3). All three $Fe(PF)(CO)_2$ structures have bent two-electron donor PF groups and can be derived from the trigonal bipyramidal $Fe(PF)(CO)_4$ structure **14−1S** by removal of different pairs of CO ligands.

Figure 3 shows that the B3LYP and BP86 functionals, which are constructed in very different ways, predict quite different singlet−triplet splittings. The triplet structure **12−2T** lies 11.6 kcal/mol *above* the singlet structure **12−1S** predicted by the BP86 method, but 2.1 kcal/mol *below* **12−1S** by the B3LYP method. The other triplet $Fe(PF)(CO)_2$ structure **12−1T** lies 8.1 kcal/mol *above* **12−1S** by the BP86 method but 1.7 kcal/mol *below* **12−1S** by the B3LYP method. This is not surprising, since Reiher and collaborators[44] have found that B3LYP always favors the high-spin state while BP86 favors the low-spin state for a series of Fe(II)-S complexes. For this reason, they proposed a new parametrization for the B3LYP functional,

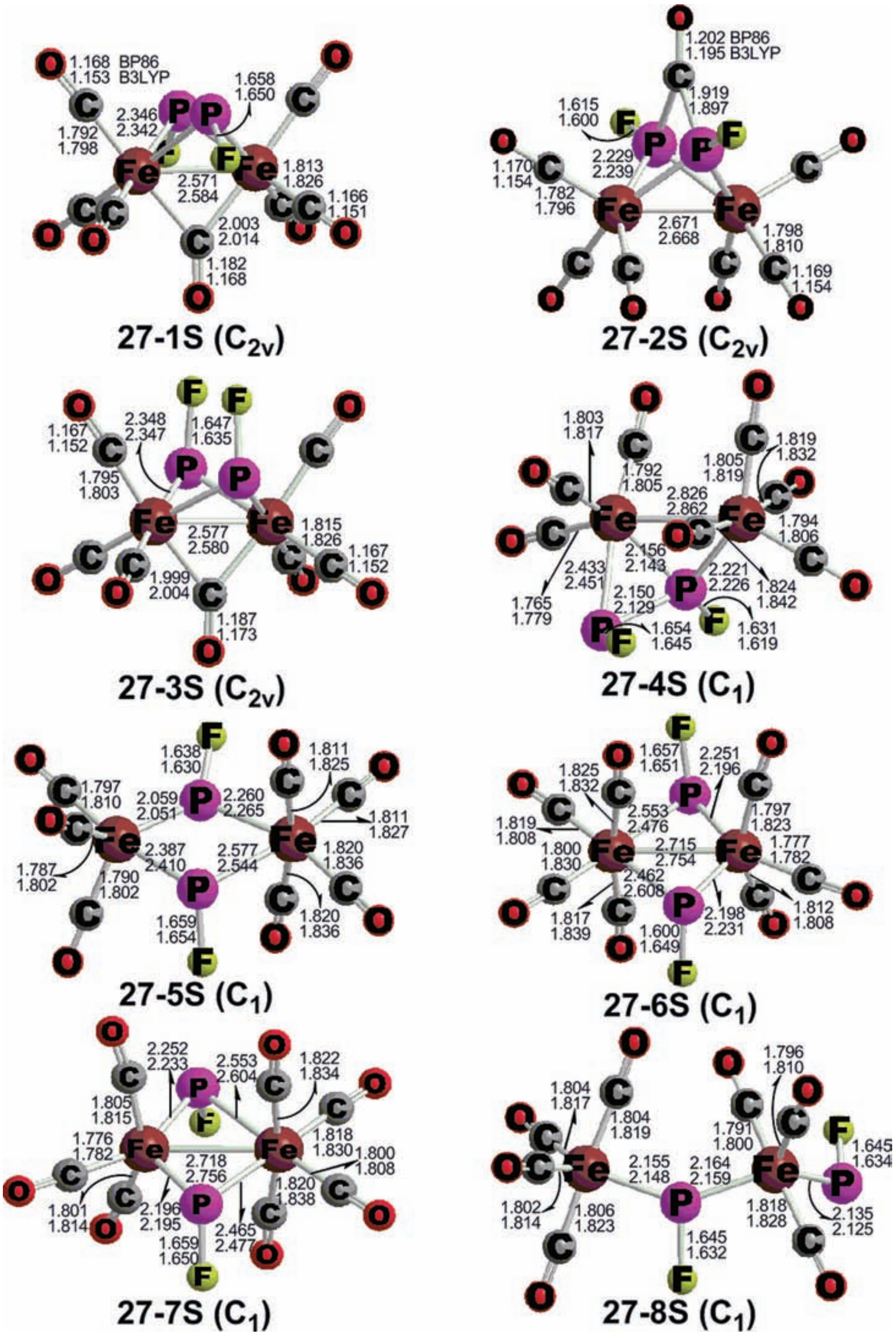


Figure 5. Eight optimized $Fe_2(PF)_2(CO)_7$ structures.

named B3LYP*, which provides electronic state orderings in agreement with experiment. In addition, these same authors have tested the B3LYP* functional with the G2 test set and obtain satisfactory results.[45] To solve the singlet−triplet splittings problem for the $Fe(PF)(CO)_n$ (n = 3, 2) isomers, we also used the B3LYP* method to get the reliable relative energies for $Fe(PF)(CO)_n$ (n = 3, 2) singlet and triplet isomers. On the basis of the B3LYP* results, structure **12−1S** is the global minimum, while structures **12−1T** and **12−2T** have relative energies of 2.1 and 2.7 kcal/mol above the **12−1S** structure, and these values are between that by B3LYP and that by BP86. With the B3LYP* method, **13−1S** is the lowest energy isomer of $Fe(PF)(CO)_3$, with structures **13−2S**, **13−1T**, and **13−2T** having the relative energies of 0.3, 11.5, and 11.0 kcal/mol, respectively, above **13−1S**, and these B3LYP* values are also between the B3LYP results and the BP86 results.

3.2. Binuclear Derivatives.

3.2.1. $Fe_2(PF)(CO)_8$. The well-known $Fe_2(CO)_9$ has a structure in which two $Fe(CO)_3$ units are linked by an iron−iron bond bridged by three carbonyl groups.[17] Replacement of one of the bridging CO groups in this $Fe_2(CO)_6(\mu\text{-}CO)_3$ structure with a PF group gives the lowest energy $Fe_2(PF)(CO)_8$ structure **28−1S** by the BP86 method (Figure 4 and Table 1). The bridging PF group in **28−1S** is a bent PF group with an angle of 71.2° between the P−F bond and the Fe−P−Fe plane. The Fe−Fe distance of 2.552 Å is very close to the experimental Fe−Fe distance[17] of

2.523 Å in $Fe_2(CO)_9$. This suggests a formal single Fe−Fe bond, thereby giving both iron atoms in **28−1S** the favored 18-electron configuration.

Attempts to optimize a triply bridged $Fe_2(CO)_6(\mu\text{-}PF)(\mu\text{-}CO)_2$ structure analogous to the BP86 structure **28−1S** using the B3LYP method led to an imaginary vibrational frequency of 34*i* cm^{-1}. Following the normal mode corresponding to this imaginary frequency breaks the two CO bridges leading to a structure bridged only by the PF group (Figure 4 and Table 1). This structure is the global minimum by the B3LYP method. In this B3LYP structure **28−1S** the out-of-plane angle between the P−F bond and the Fe−P−Fe plane is 69.9°, implying a two-electron PF donor. The Fe−Fe bond distance in the singly bridged B3LYP structure **28−1S** is predicted to be 2.772 Å, which is ~0.22 Å longer than the Fe−Fe distance in the triply bridged BP86 structure **28−1S**, but still in the range of a formal single bond. The shorter Fe−Fe distance in the triply bridged BP86 structure **28−1S** relative to that in the singly bridged B3LYP structure **28−1S** is a typical effect of increasing the number of ligands bridging a metal−metal bond of a given order.

The other $Fe_2(PF)(CO)_8$ structure found in this work, namely, **28−2S**, is a relatively high energy structure lying 24.9 kcal/mol (BP86) or 25.9 kcal/mol (B3LYP) in energy above the global minimum **28−1S** (Figure 4 and Table 1). Structure **28−2S**, like the B3LYP structure **28−1S**, has a single bridging group, but in **28−2S** the bridging group is a CO group rather than a PF group. The terminal PF ligand is a bent PF ligand and thus a two-electron donor. The Fe−Fe distance in **28−2S** of 2.785 Å (BP86) or 2.815 Å (B3LYP) is consistent with the formal single bond required to give both iron atoms the favored 18-electron configuration. The relatively high energy of the CO-bridged structure **28−2S** as compared with that of the PF-bridged structure **28−1S** suggests that bridging PF groups are more favorable than bridging CO groups.

3.2.2. $Fe_2(PF)_2(CO)_7$. Eight singlet structures are found for $Fe_2(PF)_2(CO)_7$ within 20 kcal/mol of the global minimum (Figure 5 and Table 1). Two of them (**27−1S** and **27−3S**) are C_{2v} triply bridged structures with two bridging PF ligands and a bridging CO ligand. Structure **27−1S** is the global minimum of $Fe_2(PF)_2(CO)_7$ by both the BP86 and the B3LYP methods. The bridging PF ligands are symmetry equivalent two-electron donors with a stereochemically active lone pair. Therefore, they lie out of the Fe−P−Fe plane with out-of-plane angles between the P−F bond and the Fe−P−Fe plane of 71.2° (BP86) or 72.2° (B3LYP). The Fe−Fe distance of 2.571 Å (BP86) or 2.584 Å (B3LYP), corresponds to a Fe−Fe single bond, thereby giving both Fe atoms the favored 18-electron configuration.

The triply bridged $Fe_2(PF)_2(CO)_7$ structure **27−3S** is analogous to **27−1S** except for the orientations of the P−F bonds relative to the two Fe−Fe−P planes (Figure 5 and Table 1). Structure **27−3S** lies 3.8 kcal/mol (BP86) or 5.3 kcal/mol (B3LYP) in energy above **27−1S**. The out-of-plane angles between the P−F bonds and the Fe−P−Fe plane are 68.7° (BP86) or 69.4° (B3LYP). The Fe−Fe bond distance in **27−3S** of 2.577 Å (BP86) or 2.580 Å (B3LYP) is very close to that in **27−1S**.

The C_{2v} structure **27−2S**, lying at the relatively low energy of 2.4 kcal/mol (BP86) or 2.0 kcal/mol (B3LYP) above **27−1S**, has two PF groups and one CO group bridging a pair of $Fe(CO)_3$ moieties (Figure 5 and Table 1). However, the CO group bridges the two PF groups rather than the two iron atoms. Thus the Fe···C distances of 3.051 Å (BP86) or 3.036 Å (B3LYP) to the phosphorus-bridging carbonyl group in **27−2S** are clearly nonbonding distances. The resulting bridging FPC(O)PF ligand is related to the $Pr^i_2NPC(O)PNPr^i_2$ ligand found in the known complex $(Pr^i_2NP)_2COFe_2(CO)_6$, synthesized by the reaction of $Na_2Fe(CO)_4$ with $Pr^i_2NPCl_2$ in diethyl ether and structurally characterized by X-ray crystallography.[46] In fact, structure **27−2S** can be derived from the known $(Pr^i_2NP)_2COFe_2(CO)_6$ structure by replacing the two diisopropylamino groups with fluorine atoms. The Fe−Fe distance of 2.671 Å (BP86) or 2.668 Å (B3LYP) in **27−2S** is somewhat longer than the experimental 2.603 Å Fe−Fe distance in $(Pr^i_2NP)_2COFe_2(CO)_6$, determined by X-ray crystallography, but nevertheless corresponds to a formal single bond. Since the bridging FPC(O)PF ligand in **27−2S** donates three electrons to each iron atom, both iron atoms in **27−2S** have the favored 18-electron configuration.

The $Fe_2(PF)_2(CO)_7$ structure **27−4S**, lying 6.3 kcal/mol (BP86) or 0.6 kcal/mol (B3LYP) above the global minimum, is also unusual since the two PF ligands have coupled to form a difluorodiphosphene (P_2F_2) ligand with a P−P bond distance of 2.150 Å (BP86) or 2.129 Å (B3LYP) (Figure 5 and Table 1). This difluorodiphosphene ligand in **27−4S** is unsymmetrically bonded to the Fe_2 unit with one phosphorus atom bridging both iron atoms but the other phosphorus atom bonded only to a single iron atom (the "left" iron atom in Figure 5). The bridging difluorodiphosphene ligand donates a total of four electrons to the Fe_2 unit. The Fe−Fe distance of 2.826 Å (BP86) or 2.862 Å (B3LYP) can be interpreted as a formal single bond, thereby giving both iron atoms the favored 18-electron configuration.

Three doubly PF-bridged $Fe_2(PF)_2(CO)_7$ structures, namely, **27−5S**, **27−6S**, and **27−7S**, are found within 20 kcal/mol of the global minimum **27−1S** (Figure 5 and Table 1). Structure **27−5S**, lying 10.7 kcal/mol (BP86) or 6.2 kcal/mol (B3LYP) in energy above the global minimum, has a very long Fe···Fe distance of 3.761 Å (BP86) or 3.749 Å (B3LYP) indicating the absence of a direct iron−iron bond. The fluorine atom of one of the bridging PF ligands in **27−5S** (the lower one in Figure 5) bends out of the P−Fe−Fe plane with an angle of 69.4° (BP86) or 70.6° (B3LYP), indicating a two-electron PF donor (Figure 2). However, the other bridging PF group (the upper one in Figure 5) lies almost in the P−Fe−Fe plane with an angle between the PF bond and the P−Fe−Fe plane of only 5.8° (BP86) or 4.5° (B3LYP), indicating that this PF group is a four-electron donor (Figure 2). The presence of one two-electron donor bridging PF ligand and one four-electron donor bridging PF ligand and the absence of a direct iron−iron bond gives both iron atoms in **27−5S** the favored 18-electron configuration.

The other two $Fe_2(PF)_2(CO)_7$ structures with two bridging PF groups, namely, **27−6S** and **27−7S**, are higher energy structures with essentially the same energy, namely, 15.5 kcal/mol (BP86) or 12.8 kcal/mol (B3LYP) above the global minimum (Figure 5 and Table 1). They may be considered as a pair of trans and cis isomers. Thus structure **27−6S** is the trans isomer with the fluorine atoms of the two bridging PF ligands pointing in opposite directions. Structure **27−7S** is the corresponding cis isomer in which the fluorine atoms of the two bridging PF ligands point in the same direction. In both structures, the PF ligands bend out the Fe−P−Fe planes by ~70°, indicating two-electron PF donors. The Fe−Fe distances of ~2.72 Å (BP86) and ~2.75 Å (B3LYP) in the doubly bridged structures **27−6S** and **27−7S** are significantly longer

Table 2. ν(CO) and ν(PF) Vibrational Frequencies (in cm^{-1}) and Infrared Intensities (in km/mol, Given in Parentheses) of the $Fe_2(PF)(CO)_8$ and $Fe_2(PF)_2(CO)_7$ Complexes at the BP86/DZP Level[a]

struct.	ν(CO)	ν(PF)
28−1S	*1864 (668), 1891 (183)*, 2007 (1), 2011 (7), 2011 (1181), 2016 (1258), 2041 (1704), 2073 (48)	*732 (131)*
28−2S	*1851 (431)*, 1975 (129), 1979 (89), 2002 (894), 2009 (1572), 2013 (469), 2023 (723), 2078 (339)	756 (188)
27−1S	*1898 (388)*, 2010 (25), 2012 (0), 2013 (1090), 2016 (1082), 2043 (1697), 2068 (92)	*721 (249), 729 (4)*
27−2S	*1798 (543)*, 1984 (88), 1986 (0), 1995 (861), 2004 (1109), 2022 (1697), 2057 (377)	***823 (312), 840 (63)***
27−3S	*1873 (404)*, 2004 (0), 2008 (1085), 2009 (8), 2014 (1193), 2039 (1730), 2063 (41)	*725 (19), 759 (218)*
27−4S	1972 (203), 1979 (317), 2009 (428), 2012 (1269), 2020 (280), 2022 (1507), 2076 (420)	726 (117), ***791 (191)***
27−5S	1980 (619), 1991 (574), 2017 (1021), 2017 (706), 2030 (1676), 2031 (127), 2078 (248)	*720 (122)*, ***770 (180)***
27−6S	1971 (467), 1980 (281), 2015 (513), 2021 (545), 2024 (1227), 2027 (1113), 2079 (152)	*716 (144), 724 (112)*
27−7S	1966 (394), 1984 (364), 2015 (522), 2017 (833), 2025 (1069), 2031 (954), 2080 (161)	*716 (145), 728 (118)*
27−8S	1989 (294), 1994 (258), 2000 (1325), 2005 (1197), 2013 (655), 2031 (908), 2071 (377)	***747 (143)***, 755 (182)

[a]The frequencies of bridging groups are given in *italics*. [b]*xxxx* (in italics) means bridging CO or PF groups; ***xxxx*** (in italics and bold) means four-electron donor bridging PF groups.

than the Fe−Fe distances of ∼2.57 Å in the triply bridged $Fe_2(PF)_2(CO)_7$ structures **27−1S** and **27−3S**, but still suggest the formal single bonds to give the Fe atoms the favored 18-electron configuration.

Structure **27−8S** is a still higher energy $Fe_2(PF)_2(CO)_7$ structure, lying 19.2 kcal/mol (BP86) or 15.8 kcal/mol (B3LYP) above the global minimum **27−1S** (Figure 5 and Table 1). Similar to structure **27−5S**, the long Fe···Fe distance of 4.063 Å (BP86) or 4.065 Å (B3LYP) in **27−8S** indicates the absence of an iron−iron bond. The out-of-plane angle between the bridging PF ligand in **27−8S** and the Fe−P−Fe plane is very small (7.7° by both methods), indicating a four-electron donor bridging PF group. The combination of one four-electron donor bridging PF group, one two-electron donor terminal PF group, and the absence of an iron−iron bond gives both iron atoms in **27−8S** the favored 18-electron configuration.

3.3. ν(CO) and ν(PF) Vibrational Frequencies.

Table 2 summarizes our predicted ν(CO) and ν(PF) frequencies for the $Fe_2(PF)(CO)_8$ and $Fe_2(PF)_2(CO)_7$ structures using the BP86 method, which has been shown to be more reliable than the B3LYP method for such infrared frequencies.[21,47] The terminal ν(CO) frequencies for all $Fe_2(PF)(CO)_8$ and $Fe_2(PF)_2(CO)_7$ structures fall in a typical range, namely, 2080 to 1966 cm^{-1}. The bridging ν(CO) frequencies are significantly lower than the terminal ν(CO) frequencies in accord with expectation. Thus the CO groups bridging the two iron atoms in structures **28−1S**, **28−2S**, **27−1S**, and **27−3S** exhibit ν(CO) frequencies in the range 1898 to 1851 cm^{-1}. The ν(CO) frequency for the CO group bridging the two phosphorus atoms in **27−2S** is even lower at 1798 cm^{-1}. This compares with the experimental ν(CO) frequency of 1720 cm^{-1} for the phosphorus-bridging carbonyl group in the closely related $(Pr^i{}_2N)_2COFe_2(CO)_6$.[46] The difference between this ν(CO) frequency of 1798 cm^{-1} in the $(FP)_2COFe_2(CO)_6$ structure **28−2S** and the experimental ν(CO) frequency of 1720 cm^{-1} in $(Pr^i{}_2N)_2COFe_2(CO)_6$ can relate to the substitution of the strongly electron-withdrawing fluorine atoms with the electron releasing diisopropylamino groups.

In the fluorophosphinidene structures reported in this paper, the PF groups are most frequently two-electron donor bridging ligands. The ν(PF) frequencies of such ligands are found to occur in the range from 759 to 716 cm^{-1}. Significantly higher ν(PF) frequencies of 840 and 823 cm^{-1} are found in the phosphorus-bridging carbonyl structure $(FP)_2COFe_2(CO)_6$ (**27−2S**), presumably owing to the electron-withdrawing effect of the phosphorus-bridging carbonyl group. The unsymmetrical bridging difluorodiphosphene ligand in the $Fe_2(\mu\text{-}P_2F_2)(CO)_7$ structure **27−4S** exhibits ν(PF) frequencies at 726 and 791 cm^{-1}. The ν(PF) frequency of a four-electron donor PF group bridging two iron atoms appears to depend on the number of bridging groups. Thus the ν(PF) frequency of the four-electron donor bridging PF group in the doubly bridged structure **27−5S** is 770 cm^{-1}, which is significantly higher than the 747 cm^{-1} frequency of the four-electron donor bridging PF group in the singly bridged structure **27−8S**. The terminal ν(PF) frequencies in **27−8S** and **28−2S** are 755 and 756 cm^{-1}, respectively.

3.4. Dissociation Energies.

Table 3 compares the carbonyl dissociation energies with the energies for dissociation into mononuclear fragments for $Fe_2(PF)_x(CO)_{9-x}$ (x = 0, 1, 2). These species are seen to have relatively high CO dissociation energies in excess of 23 kcal/mol. These CO dissociation energies are close to those of the well-known stable mononuclear homoleptic metal carbonyls which as indicated by the experimental carbonyl dissociation energies are 27 kcal/mol, 41 kcal/mol, and 37 kcal/mol for $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$, respectively.[48]

Table 3. .Different Kinds of Dissociation Energies (kcal/mol) for the Lowest Energy Structures of the $Fe_2(PF)(CO)_8$ and $Fe_2(PF)_2(CO)_7$ Complexes

process	BP86	B3LYP
$Fe_2(PF)_2(CO)_7 \rightarrow Fe_2(PF)_2(CO)_6 + CO$	31.4	23.3
$Fe_2(PF)_2(CO)_7 \rightarrow Fe(PF)(CO)_4 + Fe(PF)(CO)_3$	55.4	47.6
$Fe_2(PF)(CO)_8 \rightarrow Fe(PF)(CO)_4 + Fe(CO)_4$ ($^1A_1$)	49.1	40.6
$Fe_2(PF)(CO)_8 \rightarrow Fe(PF)(CO)_3 + Fe(CO)_5$	36.8	30.2
$Fe_2(CO)_9 \rightarrow Fe_2(CO)_8 + CO$	35.1[51]	29.4[51]
$Fe_2(CO)_9 \rightarrow Fe(CO)_5 + Fe(CO)_4$ ($^1A_1$)	28.3[51]	13.1[51]

A characteristic feature of the chemistry of $Fe_2(CO)_9$ is its facile dissociation into stable $Fe(CO)_5$ and a reactive $Fe(CO)_4$ fragment. This is useful for the synthesis of various $LFe(CO)_4$ derivatives by reactions of $Fe_2(CO)_9$ with the ligand L under mild conditions.[49,50] The B3LYP method predicts a relatively low energy of 13.1 kcal/mol for the dissociation of $Fe_2(CO)_9$ into the singlet products $Fe(CO)_5$ + $Fe(CO)_4$ (Table 3)[51] consistent with this experimental observation. However, both DFT methods predict significantly higher energies for analogous dissociation reactions of $Fe_2(PF)(CO)_8$ and $Fe_2(PF)_2(CO)_7$ into mononuclear fragments. This suggests that neither $Fe_2(PF)(CO)_8$ nor $Fe_2(PF)_2(CO)_7$ is likely to be a useful source of reactive $Fe(PF)(CO)_3$ fragments under mild conditions.

4. CONCLUSIONS

The fluorophosphinidene (PF) ligand functions either as a bent two-electron donor with a nonbonded stereochemically active lone pair or as a linear four-electron donor in which four of the five phosphorus valence electrons participate in the ligand−metal bonding. The bent two-electron donor PF ligand is found much more frequently than the linear four-electron donor PF ligand in the low-energy structures, even when the structures are coordinatively unsaturated.

The mononuclear tetracarbonyl $Fe(PF)(CO)_4$ is predicted to have a trigonal bipyramidal structure analogous to $Fe(CO)_5$ but with a bent PF ligand replacing one of the equatorial CO groups. The tricarbonyl $Fe(PF)(CO)_3$ is predicted to have two low-energy singlet structures, namely, one with a bent PF ligand and a 16-electron iron configuration and one with a linear PF ligand and the favored 18-electron iron configuration. This suggests a highly fluxional system for $Fe(PF)(CO)_3$. Triplet spin state $Fe(PF)(CO)_3$ structures lie at significantly higher energies than the lowest-energy singlet spin state structures. The low-energy structures for the dicarbonyl $Fe(PF)(CO)_2$ have bent PF ligands and triplet spin multiplicities. They can be derived from the $Fe(PF)(CO)_3$ structure with a bent PF ligand by removal of a CO group in two different ways.

The binuclear derivatives $Fe_2(PF)(CO)_8$ and $Fe_2(PF)_2(CO)_7$ can be regarded as analogues of the well-known $Fe_2(CO)_9$. In fact, the lowest energy $Fe_2(PF)(CO)_8$ and $Fe_2(PF)_2(CO)_7$ structures are triply bridged structures like the experimental triply bridged $Fe_2(CO)_9$ structure. The three bridges in these structures include all of the PF groups, suggesting that PF bridges are more favorable than CO bridges. In addition, the singly CO-bridged structure $Fe_2(PF)(CO)_7(\mu\text{-}CO)$ lies ~26 kcal/mol above the corresponding singly PF-bridged structure $Fe_2(CO)_8(\mu\text{-}PF)$.

The presence of two PF groups in $Fe_2(PF)_2(CO)_7$ leads to other types of interesting structures lying at energies close to the triply bridged structures noted above. For example, a phosphorus-bridging carbonyl group is found in an $(FP)_2COFe_2(CO)_6$ structure, lying only ~2 kcal/mol above the global minimum. This structure is related to the very stable dialkylaminophosphinidene derivative $(Pr^i{}_2NP)_2COFe_2(CO)_6$, which can be readily synthesized in large quantities.[46] The two PF ligands also can couple to form a difluorodiphosphene (P_2F_2) ligand in another low energy structure, described as $Fe_2(CO)_7(\mu\text{-}P_2F_2)$. In this structure the P_2F_2 ligand is bonded unsymmetrically to the Fe_2 unit so that one iron atom is bonded to two phosphorus atoms but the other iron atom is bonded only to a single phosphorus atom.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table **S1**: The vibrational frequencies and infrared intensities of the $Fe_2(PF)(CO)_8$ and $Fe_2(PF)_2(CO)_7$ complexes at the BP86/DZP level; Table **S2−S3**: The Cartesian coordinates of the optimized $Fe_2(PF)(CO)_8$ and $Fe_2(PF)_2(CO)_7$ structures at the BP86/DZP and B3LYP/DZP levels; complete Gaussian 03 reference (Reference 43). This material is available free of charge via the Internet at http://pubs.acs.org.

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