

# Unexpected Direct Iron-Fluorine Bonds in Trifluorophosphane Iron Complexes: An Alternative to Bridging Trifluorophosphane and Difluorophosphido Groups

Rong Zou,<sup>[a]</sup> Qian-shu Li,<sup>\*,[a, b]</sup> Yaoming Xie,<sup>[c]</sup> R. Bruce King,<sup>\*,[a, c]</sup> and Henry F. Schaefer III<sup>[c]</sup>

**Abstract:** The iron trifluorophosphane complexes  $[\text{Fe}(\text{PF}_3)_n]$  ( $n=4, 5$ ),  $[\text{Fe}_2(\text{PF}_3)_n]$  ( $n=8, 9$ ),  $[\text{H}_2\text{Fe}(\text{PF}_3)_4]$ , and  $[\text{Fe}_2(\text{PF}_2)_2(\text{PF}_3)_6]$  have been studied by density functional theory. The lowest energy structures of  $[\text{Fe}(\text{PF}_3)_4]$  and  $[\text{Fe}(\text{PF}_3)_5]$  are a triplet tetrahedron and a singlet trigonal bipyramid, respectively. Both *cis* and *trans* octahedral structures were found for  $[\text{H}_2\text{Fe}(\text{PF}_3)_4]$  with the *cis* isomer lying lower in energy by  $\approx 10 \text{ kcal mol}^{-1}$ . The lowest energy structure for  $[\text{Fe}_2(\text{PF}_3)_8]$  has two  $[\text{Fe}(\text{PF}_3)_4]$  units linked only by an iron-iron bond of length 2.505 Å consistent with the formal Fe=Fe double bond

required to give both iron atoms the favored 18-electron configuration. In the lowest energy structure for  $[\text{Fe}_2(\text{PF}_3)_9]$  one of the iron atoms has inserted into a P–F bond of one of the  $\text{PF}_3$  ligands to give a structure  $[(\text{F}_3\text{P})_4\text{Fe} \leftarrow \text{PF}_2\text{Fe}(\text{F})(\text{PF}_3)_4]$  with a bridging  $\text{PF}_2$  group and a direct Fe–F bond. A bridging  $\text{PF}_3$  group is found in a considerably higher energy  $[\text{Fe}_2-$

$(\text{PF}_3)_9]$  structure at  $\approx 30 \text{ kcal mol}^{-1}$  above the global minimum. However, this bridging  $\text{PF}_3$  group keeps the two iron atoms too far apart ( $\approx 4 \text{ \AA}$ ) for the direct iron-iron bond required to give the iron atoms the favored 18-electron configuration. The preferred structure for  $[\text{Fe}_2(\text{PF}_2)_2(\text{PF}_3)_6]$  has a bridging  $\text{PF}_2$  group, as expected. However, this bridging  $\text{PF}_2$  group bonds to one of the iron atoms through an P–Fe covalent bond and to the other iron through an F→Fe dative bond, leaving an uncomplexed phosphorus lone pair.

**Keywords:** density functional calculations • iron • metal–metal interactions • phosphane ligands • trifluorophosphane

## Introduction

Development of the chemistry of homoleptic metal trifluorophosphane complexes<sup>[1]</sup>  $[\text{M}(\text{PF}_3)_n]$  parallels that of metal carbonyls, but is much more recent in origin. Thus the first homoleptic metal carbonyl to be discovered was  $[\text{Ni}(\text{CO})_4]$ , which was first synthesized in 1890 by the reaction of finely divided nickel with carbon monoxide at atmospheric CO pressure.<sup>[2]</sup> However,  $[\text{Ni}(\text{CO})_4]$  was subsequently found to be almost the only binary metal carbonyl that can be synthesized efficiently at atmospheric CO pressure. Thus reactions in autoclaves at high CO pressures were found to be necessary for the synthesis of other metal carbonyls including the very important  $[\text{Fe}(\text{CO})_5]$ ,  $[\text{Mo}(\text{CO})_6]$ , and  $[\text{Co}_2(\text{CO})_8]$ , discovered about a century ago and now commercially available for many years. Analogously, the first homoleptic metal trifluorophosphane complex was  $[\text{Ni}(\text{PF}_3)_4]$ , which was first reported in 1951 by Irvine and Wilkinson,<sup>[3,4]</sup> who synthesized it from  $[\text{Ni}(\text{P}(\text{Cl})_2)_4]$  and excess  $\text{PF}_3$ . Further extensive development of homoleptic metal trifluorophosphane chemistry required the development of techniques for performing reactions at elevated  $\text{PF}_3$  pressure with Kruck and

[a] R. Zou, Prof. Q.-s. Li, Prof. R. B. King  
Center for Computational Quantum Chemistry  
South China Normal University  
Guangzhou 510631 (P. R. China)  
Fax: (+86)20-39310439  
E-mail: rbking@chem.uga.edu

[b] Prof. Q.-s. Li  
Institute of Chemical Physics  
Beijing Institute of Technology  
Beijing 100081 (P. R. China)  
Fax: (+86)10-68912665

[c] Dr. Y. Xie, Prof. R. B. King, Prof. H. F. Schaefer, III  
Department of Chemistry and Center  
for Computational Chemistry  
University of Georgia  
Athens, Georgia 30602 (USA)  
Fax: (+1)706-542-0406

Supporting information for this article—Tables S1–S11. Harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ) and infrared intensities (in  $\text{km/mol}$ ) for the  $[\text{Fe}(\text{PF}_3)_4]$ ,  $[\text{Fe}(\text{PF}_3)_5]$ ,  $[\text{H}_2\text{Fe}(\text{PF}_3)_4]$ ,  $[\text{Fe}_2(\text{PF}_3)_8]$ ,  $[\text{Fe}_2(\text{PF}_2)_2(\text{PF}_3)_6]$ , and  $[\text{Fe}_2(\text{PF}_3)_9]$  structures; Tables S12–S22. Atomic coordinates of the optimized structures of  $[\text{Fe}(\text{PF}_3)_4]$ ,  $[\text{Fe}(\text{PF}_3)_5]$ ,  $[\text{H}_2\text{Fe}(\text{PF}_3)_4]$ ,  $[\text{Fe}_2(\text{PF}_3)_8]$ ,  $[\text{Fe}_2(\text{PF}_2)_2(\text{PF}_3)_6]$ , and  $[\text{Fe}_2(\text{PF}_3)_9]$ ; complete Gaussian 03 reference (Reference 51)—is available on the WWW under <http://dx.doi.org/10.1002/chem.200801248>.

co-workers being the pioneers in this area.<sup>[5]</sup> This was very challenging work from an experimental point of view, owing to the need for large amounts of high purity PF<sub>3</sub> to generate the necessary pressures in the reaction autoclaves. Using such reactions at elevated PF<sub>3</sub> pressure, certain key homoleptic metal trifluorophosphane complexes such as [Cr(PF<sub>3</sub>)<sub>6</sub>]<sup>[6]</sup> and [Pt(PF<sub>3</sub>)<sub>4</sub>]<sup>[7,8]</sup> were synthesized for the first time. Subsequently the experimentally challenging need for elevated PF<sub>3</sub> pressure in syntheses of homoleptic metal trifluorophosphane derivatives was partially superseded by methods such as reactions of metal vapors with PF<sub>3</sub> in a metal-vapor reactor<sup>[9,10]</sup> or exhaustive photolysis<sup>[11]</sup> of the corresponding metal carbonyls with PF<sub>3</sub>. In general, homoleptic neutral metal trifluorophosphane complexes were found to be rather volatile, like the corresponding metal carbonyls, despite their considerably higher molecular weights.

The trifluorophosphane ligand in metal trifluorophosphane complexes is recognized as being a strong acceptor ligand like carbon monoxide, undoubtedly because of the electron withdrawing properties of the three highly electronegative fluorine atoms.<sup>[12–21]</sup> Thus PF<sub>3</sub> ligands, like CO ligands, stabilize low formal oxidation states so that zerovalent metal derivatives, such as [Cr(PF<sub>3</sub>)<sub>6</sub>], [Fe(PF<sub>3</sub>)<sub>5</sub>], and [Ni(PF<sub>3</sub>)<sub>4</sub>], are relatively stable towards air oxidation. Furthermore, metal trifluorophosphane complexes have been found to be more stable than the corresponding homoleptic metal carbonyls. Good examples of metal trifluorophosphane complexes without stable currently known homoleptic metal carbonyl counterparts include [M<sub>2</sub>(PF<sub>3</sub>)<sub>8</sub>] (M = Rh, Ir),<sup>[22]</sup> [Pt(PF<sub>3</sub>)<sub>4</sub>]<sup>[7,8,23]</sup>, and [Pt<sub>4</sub>(PF<sub>3</sub>)<sub>8</sub>]<sup>[24]</sup>.

These observations of the higher stability of metal trifluorophosphane complexes relative to corresponding metal carbonyls suggested that metal trifluorophosphane chemistry might develop into a more extensive area of inorganic chemistry than even metal carbonyl chemistry. However, as metal trifluorophosphane chemistry continued to evolve, it became increasingly apparent that whereas metal trifluorophosphane complexes with terminal PF<sub>3</sub> groups were generally more stable than their carbonyl counterparts, metal trifluorophosphane complexes with bridging PF<sub>3</sub> groups analogous to well-known metal carbonyls with bridging carbonyl groups, such as [Fe<sub>2</sub>(CO)<sub>9</sub>] (or [Fe<sub>2</sub>(CO)<sub>6</sub>(μ-CO)<sub>3</sub>]) and Co<sub>2</sub>(CO)<sub>8</sub> (or [Co<sub>2</sub>(CO)<sub>6</sub>(μ-CO)<sub>2</sub>]), remained unknown. The reasons for this instability or unfavorability of metal trifluorophosphane derivatives with bridging PF<sub>3</sub> groups has continued to remain obscure (Figure 1).

This paper describes density functional theory (DFT) studies directed towards understanding the absence of bridg-

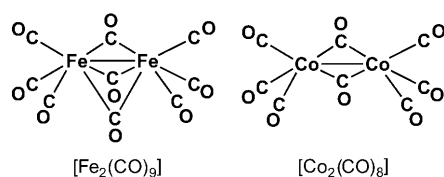


Figure 1. Two homoleptic binuclear metal carbonyls with bridging carbonyl groups with no known trifluorophosphane analogues.

ing trifluorophosphane groups in metal trifluorophosphane chemistry. Homoleptic iron trifluorophosphane iron derivatives were chosen for this study for the following reasons:

- 1) The mononuclear derivatives [Fe(PF<sub>3</sub>)<sub>5</sub>]<sup>[25,26]</sup> and [H<sub>2</sub>Fe(PF<sub>3</sub>)<sub>4</sub>]<sup>[27,28,29]</sup> are known and are reasonable starting materials to synthesize any interesting new compounds predicted by our theoretical studies;
- 2) The binuclear iron carbonyl [Fe<sub>2</sub>(CO)<sub>6</sub>(μ-CO)<sub>3</sub>] with three bridging CO groups is known<sup>[30,31]</sup> and would suggest [Fe<sub>2</sub>(PF<sub>3</sub>)<sub>6</sub>(μ-PF<sub>3</sub>)<sub>3</sub>] as a reasonable candidate for a homoleptic trifluorophosphane complex containing bridging PF<sub>3</sub> groups.

An important result from the present theoretical study is the discovery of new types of unexpected interactions between the fluorine atoms of coordinated fluorophosphanes and metal atoms in trifluorophosphane metal complexes. At least for the binuclear iron complexes investigated in this work, such interactions are predicted to occur in preference to the formation of bridging trifluorophosphane complexes analogous to well-known metal carbonyls with bridging carbonyl groups.

## Theoretical Methods

Electron correlation effects were considered by using density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds.<sup>[32–40]</sup> Thus two DFT methods were used in this study. The first functional is the B3LYP method, which is the hybrid HF/DFT method that uses a combination of the three-parameter Becke functional (B3) with the Lee-Yang-Parr (LYP) generalized gradient correlation functional.<sup>[41,42]</sup> 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).<sup>[43,44]</sup> It has been noted elsewhere that the BP86 method may be somewhat more reliable than B3LYP for the types of organometallic systems considered in this paper.<sup>[45,46,47]</sup>

All computations were performed by using double- $\zeta$  plus polarization (DZP) basis sets. The DZP basis sets used for fluorine add one set of pure spherical harmonic d functions with orbital exponents  $\alpha_d(\text{F})=1.0$  to the standard Huzinaga-Dunning contracted DZ sets<sup>[48,49]</sup> and are designated (9s5p1d/4s2p1d). The DZP basis sets used for phosphorus add a polarization d function with  $\alpha_d(\text{P})=0.6$  to Dunning's DZ (11s7p1d/6s4p1d) set.<sup>[50]</sup> 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 the transition metals is the Wachters primitive set<sup>[51]</sup> augmented by two sets of p functions and a set of d functions, contracted following Hood, Pitzer and Schaefer,<sup>[52]</sup> designated (14s11p6d/10s8p3d).

The geometries of all structures were fully optimized using the DZP B3LYP and DZP BP86 methods. 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 03 program,<sup>[53]</sup> exercising the fine grid option (75 radial shells, 302 angular points) for evaluating integrals numerically and the tight ( $10^{-8}$  hartree) designation is the default for the self-consistent field (SCF) convergence.

In the search for minima using all currently implemented DFT methods, low magnitude imaginary vibrational frequencies are suspect because of significant limitations in the numerical integration procedures used in the DFT computations.<sup>[54]</sup> Thus all imaginary vibrational frequencies with a magnitude less than  $50i\text{ cm}^{-1}$  are considered questionable, and are given less weight in the analysis.<sup>[54,55,56]</sup> Therefore, we do not always follow such low imaginary vibrational frequencies.

## Results

**Complex  $[\text{Fe}(\text{PF}_3)_4]$ :** Three structures were optimized for  $[\text{Fe}(\text{PF}_3)_4]$  (Figure 2, Table 1). Structure **1b** has two small imaginary frequencies, but the other structures are genuine minima without any imaginary frequencies. The two lowest lying structures (**1a** and **1b**) are both triplet electronic states lying within  $1.2\text{ kcal mol}^{-1}$  of each other. Both structures have approximately tetrahedral  $\text{FeP}_4$  coordination and differ only in the rotation of the  $\text{PF}_3$  ligands about the  $\text{Fe-P}$  bonds. The only singlet  $[\text{Fe}(\text{PF}_3)_4]$  structure found in this work, namely **1c** lying  $17.2\text{ kcal mol}^{-1}$  (B3LYP) or  $8.1\text{ kcal mol}^{-1}$  (BP86) above **1a**, has the same tetrahedral  $\text{FeP}_4$  coordination.

**Complex  $[\text{Fe}(\text{PF}_3)_5]$ :** The only structure found for  $[\text{Fe}(\text{PF}_3)_5]$  is the expected trigonal bipyramidal structure **II** (Figure 3, Table 2), which is a genuine minimum without any imaginary frequencies. The length of the axial  $\text{Fe-P}$  bond is  $2.160\text{ \AA}$  (B3LYP) or  $2.139\text{ \AA}$  (BP86), and that of the equatorial  $\text{Fe-P}$  bond is  $2.123\text{ \AA}$  (B3LYP) or  $2.111\text{ \AA}$  (BP86). Although  $[\text{Fe}(\text{PF}_3)_5]$  has been synthesized as a relatively stable compound,<sup>[25,26]</sup> its structure has not been determined by X-ray diffraction or other definitive method.

**Complex  $[\text{H}_2\text{Fe}(\text{PF}_3)_4]$ :** Two  $[\text{H}_2\text{Fe}(\text{PF}_3)_4]$  structures were found (Figure 4 and Table 3). The  $C_{2v}$  structure **IIIa** for  $[\text{H}_2\text{Fe}(\text{PF}_3)_4]$  is the lowest energy structure with two small imaginary frequencies, namely  $20i$  and  $9i$  (B3LYP) or  $7i$  (BP86). The  $\text{FeP}_4\text{H}_2$  coordina-

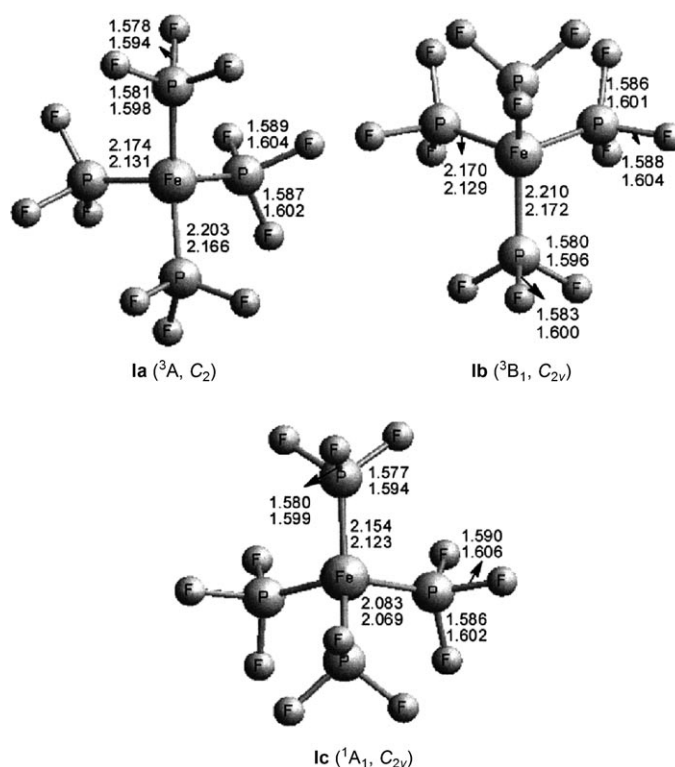


Figure 2. The three optimized  $[\text{Fe}(\text{PF}_3)_4]$  structures.

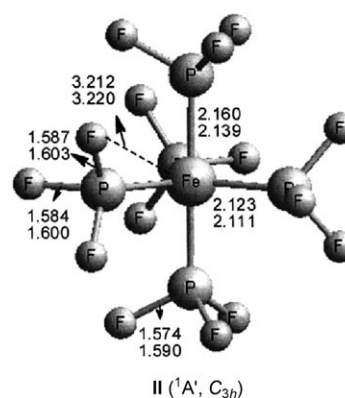


Figure 3. The optimized  $[\text{Fe}(\text{PF}_3)_5]$  structure.

Table 1. Bond distances (in  $\text{\AA}$ ), total energies ( $E$  in hartree), and relative energies ( $\Delta E$  and  $\Delta E_{\text{ZPVE}}$  in  $\text{kcal mol}^{-1}$ ) for the  $[\text{Fe}(\text{PF}_3)_4]$  structures.

	<b>1a</b> ( $C_2$ )		<b>1b</b> ( $C_{2v}$ )		<b>1c</b> ( $C_{2v}$ )	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
$\text{Fe-P}_{\text{ax}}$	2.203	2.166	2.210	2.172	2.154	2.123
$\text{Fe-P}_{\text{eq}}$	2.174	2.131	2.170	2.129	2.083	2.069
$E$	-3828.05532	-3828.33175	-3828.05360	-3828.32988	-3828.02787	-3828.31889
$\Delta E$	0.0	0.0	1.1	1.2	17.2	8.1
$\Delta E_{\text{ZPVE}}$	0.0	0.0	1.0	1.0	17.9	8.5
imaginary frequencies	none	none	$24i, 23i$	$27i, 25i$	none	none

Table 2. Bond distances (in Å) and total energies ( $E$  in hartree) for  $[\text{Fe}(\text{PF}_3)_5]$ .

	<b>II</b> ( $C_{3h}$ )	
	B3LYP	BP86
Fe–P <sub>ax</sub>	2.160	2.139
Fe–P <sub>eq</sub>	2.123	2.111
$E$	–4469.14065	–4469.45776
imaginary frequencies	none	none

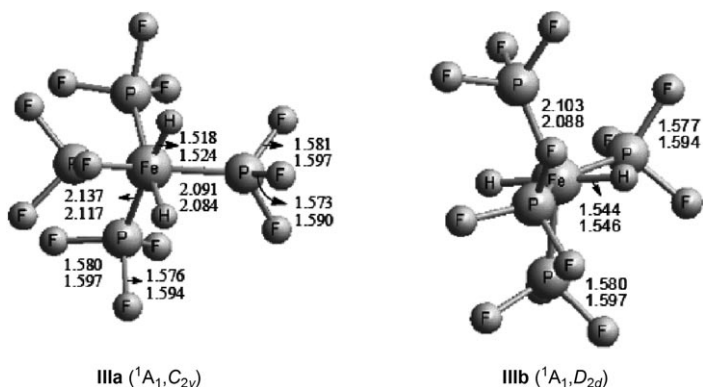


Figure 4. The two optimized  $[\text{H}_2\text{Fe}(\text{PF}_3)_4]$  structures.

Table 3. Bond distances (in Å), total energies ( $E$  in hartree), and relative energies ( $\Delta E$  and  $\Delta E_{\text{ZPVE}}$  in kcal mol<sup>-1</sup>) for the  $[\text{H}_2\text{Fe}(\text{PF}_3)_4]$  structures.

	<b>IIIa</b> ( $C_{2v}$ )		<b>IIIb</b> ( $D_{2d}$ )	
	B3LYP	BP86	B3LYP	BP86
Fe–P <sub>ax</sub>	2.137	2.117	2.103	2.088
Fe–P <sub>eq</sub>	2.091	2.084	–	–
Fe–H	1.518	1.524	1.544	1.546
H–Fe–H	87.1	86.5	180.0	180.0
$E$	–3829.27118	–3829.56700	–3829.25344	–3829.55110
$\Delta E$	0.0	0.0	11.1	10.0
$\Delta E_{\text{ZPVE}}$	0.0	0.0	10.3	9.2
imaginary frequencies	20i,9i	7i	none	none

tion geometry in **IIIa** is approximately octahedral with a *cis* arrangement of the two hydrogen atoms. The higher energy  $D_{2d}$  structure **IIIb** for  $[\text{H}_2\text{Fe}(\text{PF}_3)_4]$  at 11.1 kcal mol<sup>-1</sup> (B3LYP) or 10.0 kcal mol<sup>-1</sup> (BP86) above **IIIa** is a genuine minimum without any imaginary frequencies. The  $\text{FeP}_4$  unit in **IIIb** is a tetrahedron distorted from  $T_d$  to  $D_{2d}$ . The capping hydrogen atoms in **IIIb** have a transoid arrangement with a nearly linear H–Fe–H angle.

Although  $[\text{H}_2\text{Fe}(\text{PF}_3)_4]$  has been synthesized and some studies of its chemistry have been made,<sup>[27,29]</sup> its structure has not been determined by definitive methods, such as X-ray

crystallography. However, multinuclear NMR studies in the –70°C to +80°C temperature range suggest two interconverting isomers. In addition, the Mössbauer spectrum at –70°C has been interpreted as a mixture of *cis* and *trans* isomers, which could correspond to **IIIa** and **IIIb**, respectively.

**Complex  $[\text{Fe}_2(\text{PF}_3)_8]$ :** Two structures were found for  $[\text{Fe}_2(\text{PF}_3)_8]$ . Both structures are genuine minima without any imaginary frequencies (Figure 5, Table 4). The lower energy  $[\text{Fe}_2(\text{PF}_3)_8]$  structure **IVa** has  $D_2$  symmetry and consists of two  $[\text{Fe}(\text{PF}_3)_4]$  units linked by an unbridged iron-iron bond. The length of the iron-iron bond is 2.505 Å by either method. This result is consistent with the formal Fe=Fe double bond required to give both iron atoms the favored 18-electron configuration.

The higher energy  $[\text{Fe}_2(\text{PF}_3)_8]$  structure **IVb** (Figure 5 and Table 4) at 9.4 kcal mol<sup>-1</sup> (B3LYP) or 23.5 kcal mol<sup>-1</sup> (BP86) above **IVa** has two bridging  $\text{PF}_3$  groups and represents the

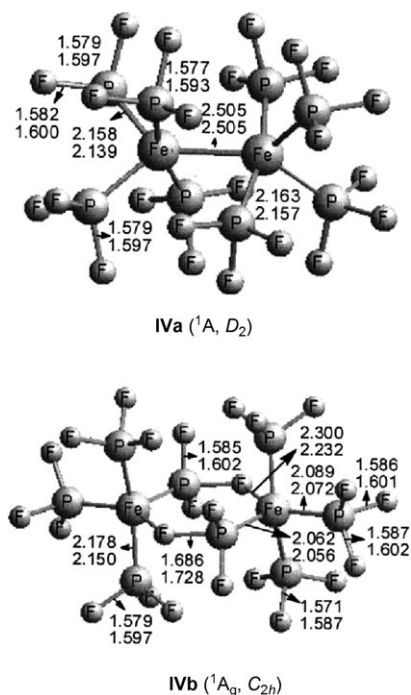


Figure 5. The two optimized  $[\text{Fe}_2(\text{PF}_3)_8]$  structures.

Table 4. Bond distances (in Å), total energies ( $E$  in hartree), and relative energies ( $\Delta E$  and  $\Delta E_{\text{ZPVE}}$  in kcal mol<sup>-1</sup>) for  $[\text{Fe}_2(\text{PF}_3)_8]$  and  $[\text{Fe}_2(\text{PF}_3)_2(\text{PF}_3)_6]$ .

	<b>IVa</b> ( $D_2$ )		<b>IVb</b> ( $C_{2h}$ )		<b>V</b> ( $C_2$ )	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Fe–Fe	2.505	2.505	4.153	4.077	2.913	2.864
Fe–P <sub>bridge</sub>	–	–	2.062	2.056	2.182	2.145
Fe–F	–	–	2.300	2.232	2.230	2.331
$E$	–7656.08187	–7656.68984	–7656.06695	–7656.65238	–7456.20057	–7456.81091
$\Delta E$	0.0	0.0	9.4	23.5	–	–
$\Delta E_{\text{ZPVE}}$	0.0	0.0	8.5	22.6	–	–
imaginary frequency	none	none	none	none	2i	none

first example of a metal trifluorophosphane structure with bridging  $\text{PF}_3$  groups. However, the bridging  $\text{PF}_3$  groups in **IVb** are fundamentally different from the bridging carbonyl groups found in metal carbonyls. Thus in most bridging carbonyl groups both metals are normally bonded to the carbonyl carbon and such bridging carbonyl groups are formally donors of two electrons. However, in the bridging  $\text{PF}_3$  groups in **IVb** one of the iron atoms is bonded to the phosphorus atom receiving two electrons from the phosphorus lone pair and the other iron atom is bonded to a fluorine atom and receives two electrons from a fluorine lone pair. Thus the two bridging  $\text{PF}_3$  groups in **IVb** are both formal four-electron donors leading to the favored 18-electron configuration for both iron atoms without any direct iron-iron bonding. This is consistent with the geometry of the  $\text{Fe}_2\text{P}_2\text{F}_2$  ring in **IVb** in which the iron atoms are in *para* positions with an  $\text{Fe}\cdots\text{Fe}$  distance of 4.153 Å (B3LYP) or 4.077 Å (BP86), which is far outside the reasonable bonding range. The coordination environment of each iron atom in **IVb** is an  $\text{FeP}_4\text{F}$  trigonal bipyramid similar to that of  $[\text{Fe}(\text{PF}_3)_5]$  (Figure 3). Two of the equatorial positions in the iron trigonal bipyramids are  $\text{Fe}-\text{P}$  and  $\text{Fe}-\text{F}$  bonds in the central  $\text{Fe}_2\text{P}_2\text{F}_2$  ring. The lengths of the  $\text{Fe}-\text{P}$  bonds in the  $\text{Fe}_2\text{P}_2\text{F}_2$  rings are 2.062 Å (B3LYP) or 2.056 Å (BP86).

**Complex  $[\text{Fe}_2(\text{PF}_2)_2(\text{PF}_3)_6]$ :** The reaction of iron vapor with  $\text{PF}_3$  has been reported<sup>[9,10]</sup> to produce  $[\text{Fe}_2(\text{PF}_2)_2(\text{PF}_3)_6]$  of unknown structure, which has been characterized only by  $^{19}\text{F}$  NMR and mass spectrometry. Our DFT studies on  $[\text{Fe}_2(\text{PF}_2)_2(\text{PF}_3)_6]$  predict a structure **V** with two unprecedented types of bridging  $\text{PF}_2$  groups in which the phosphorus atom forms a normal two center two-electron bond with one iron atom and one of the two  $\text{PF}_2$  fluorine atoms forms a dative bond to the other iron atom (Figure 6, Table 4). This is depicted schematically in Figure 7, in which the unusual  $\text{PF}_2$  group in this structure is designated as a  $\text{P},\text{F}-\eta^2-\mu-\text{PF}_2$  group to reflect the nature of its bonding to the pair of iron atoms. Note that the phosphorus lone pair is not involved in the bonding to the iron atoms in this type of bridge, undoubtedly a consequence of its weak basicity owing to the strongly electron withdrawing properties of the two fluorine atoms. In the bridging  $\text{P},\text{F}-\eta^2-\mu-\text{PF}_2$  group to the iron atoms in **V**,

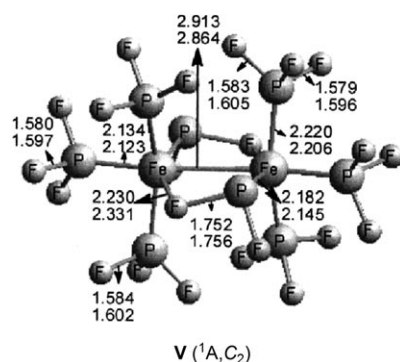


Figure 6. The optimized  $[\text{Fe}_2(\text{P},\text{F}-\eta^2-\mu-\text{PF}_2)_2(\text{PF}_3)_6]$  structure.

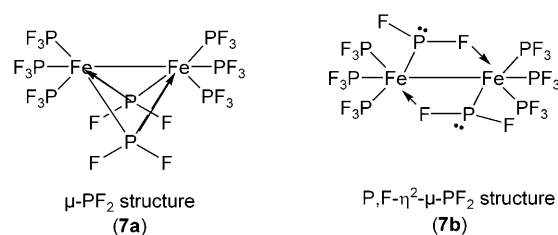


Figure 7. Alternative modes of  $\text{PF}_2$  bridging in  $[\text{Fe}_2(\mu-\text{PF}_2)_2(\text{PF}_3)_6]$ .

the  $\text{P}-\text{Fe}$  distances are 2.182 Å (B3LYP) or 2.145 Å (BP86) and the  $\text{F}\rightarrow\text{Fe}$  distances are 2.230 Å (B3LYP) or 2.331 Å (BP86). The  $\text{Fe}-\text{Fe}$  bond in **V** is relatively long at 2.913 Å (B3LYP) or 2.864 Å (BP86) because of the geometry of the  $\text{Fe}_2\text{P}_2\text{F}_2$  ring. Figure 7 also contrasts the unusual structure of **V** with the  $[\text{Fe}_2(\mu-\text{PF}_2)_2(\text{PF}_3)_6]$  structure that might have been expected *a priori* by analogy with the numerous known  $[\text{Fe}_2(\text{PR}_2)_2(\text{CO})_6]$  derivatives as well as the known<sup>[57]</sup> related  $[\text{Co}_2(\text{PF}_2)_2(\text{PF}_3)_6]$ . Thus in structure **7a** in Figure 7 the bridging phosphorus atoms are tetracoordinate with no lone pairs and there are no iron-fluorine bonds. However, in structure **7b** the bridging phosphorus atoms are tricoordinate with a lone pair each and there is one iron-fluorine bond for each  $\text{PF}_2$  group. A structure of the type **7a** (Figure 7) for  $[\text{Fe}_2(\text{PF}_2)_2(\text{PF}_3)_6]$  was found by the DFT methods used in this paper to lie at a very high energy ( $\approx 70 \text{ kcal mol}^{-1}$ ) above **V** (Figure 6) and to have a significant imaginary vibrational frequency ( $\approx 200i \text{ cm}^{-1}$ ).

**Complex  $[\text{Fe}_2(\text{PF}_3)_9]$ :** Two structures for  $[\text{Fe}_2(\text{PF}_3)_9]$  were found (Figure 8, Table 5). Both structures have small imaginary frequencies, namely  $7i$  (B3LYP) or  $8i \text{ cm}^{-1}$  (BP86) for **VIa**, and  $20i$  (B3LYP) or  $26i$  and  $9i \text{ cm}^{-1}$  (BP86) for **VIb**. In the global minimum  $[\text{Fe}_2(\text{PF}_3)_9]$  structure one of the iron atoms (the “right” iron atom in Figure 8) has inserted into the  $\text{P}-\text{F}$  bond of a trifluorophosphane ligand to give an  $\text{Fe}-\text{F}$  bond of length 1.904 Å (B3LYP) or 1.925 Å (BP86) as well as a  $\text{PF}_2$  group with a  $\text{P}-\text{Fe}$  bond length of 2.194 Å (B3LYP) or 2.177 Å (BP86), leading to a +2 formal oxidation state for this iron atom. This  $\text{PF}_2$  group coordinates to the other iron atom (the “left” iron atom in Figure 8) through the phosphorus lone pair with a  $\text{P}\rightarrow\text{Fe}$  bond length of 2.378 Å (B3LYP) or 2.399 Å (BP86). The left iron atom has a five-coordinate  $\text{FeP}_5$  environment, which is a distorted version of the trigonal bipyramidal iron environment in  $[\text{Fe}(\text{PF}_3)_5]$  and corresponds to iron(0). Thus in **VIa** one iron atom has a five-coordinate environment and the other iron atom has a six-coordinate environment. Each iron atom in **VIa** has the favored 18-electron configuration, without requiring an iron-iron bond consistent with the long non-bonding  $\text{Fe}\cdots\text{Fe}$  distance of 4.111 Å (B3LYP) or 4.085 Å (BP86).

The second structure found for  $[\text{Fe}_2(\text{PF}_3)_9]$ , namely **VIb**, has an intact bridging  $\text{PF}_3$  group, but lies at the high energy of  $32.0 \text{ kcal mol}^{-1}$  (B3LYP) or  $27.9 \text{ kcal mol}^{-1}$  (BP86) above **VIa**. In **VIb** both iron atoms are bonded to the phosphorus



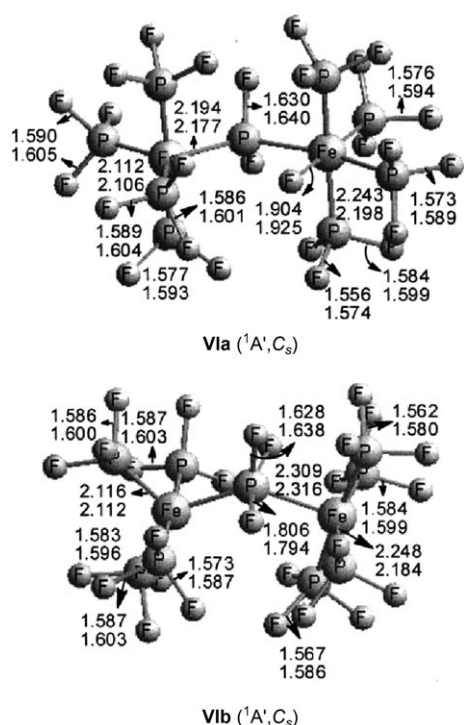


Figure 8. The two optimized  $[\text{Fe}_2(\text{PF}_3)_9]$  structures.

Table 5. Bond distances (in Å), total energies ( $E$  in hartree), and relative energies ( $\Delta E$  and  $\Delta E_{\text{ZPVE}}$  in  $\text{kcal mol}^{-1}$ ) for the two  $[\text{Fe}_2(\text{PF}_3)_9]$  structures.

	<b>VIa</b> ( $C_s$ )		<b>VIb</b> ( $C_s$ )	
	B3LYP	BP86	B3LYP	BP86
Fe–Fe	4.111	4.085	4.233	4.187
Fe–P <sub>bridge</sub>	2.194/2.378	2.177/2.399	2.249/2.309	2.253/2.316
Fe–P–Fe	128.0	126.3	136.4	132.9
$E$	–8297.16873	–8297.77811	–8297.11771	–8297.73361
$\Delta E$	0.0	0.0	32.0	27.9
$\Delta E_{\text{ZPVE}}$	0.0	0.0	31.4	27.0
imaginary frequency	7i	8i	20i	26i, 9i

atom of the bridging  $\text{PF}_3$  group leading to distorted trigonal bipyramidal coordination with the iron atoms in axial positions. The iron-iron distance in **VIb** at 4.233 Å (B3LYP) or 4.187 Å (BP86) is far too long for a direct iron-iron bond. This long  $\text{Fe}\cdots\text{Fe}$  distance makes the bridging  $\text{PF}_3$  group different from the bridging carbonyl groups in most metal carbonyls, including  $[\text{Fe}_2(\text{CO})_9]$  (Figure 1), where the bridging carbonyl group is accompanied by a metal–metal distance consistent with bonding.

**Vibrational frequencies:** The calculated  $\nu(\text{PF})$  frequencies for the compounds discussed in this paper using the BP86 method are listed in Table 6, including comparison with the experimental values for the known compounds  $[\text{Fe}(\text{PF}_3)_5]$ ,  $[\text{H}_2\text{Fe}(\text{PF}_3)_4]$ , and  $[\text{Fe}_2(\text{PF}_3)_6(\text{PF}_2)_2]$ . The terminal  $\nu(\text{PF})$  frequencies were found in the broad range 750 to 920  $\text{cm}^{-1}$ .

The bridging  $\nu(\text{PF})$  frequencies in the  $\text{P–F}\rightarrow\text{Fe}$  units in the binuclear derivatives **IVb**, **V**, and **VIb** are significantly lower in the range 515 to 560  $\text{cm}^{-1}$  just as bridging  $\nu(\text{CO})$  frequencies are significantly lower than terminal  $\nu(\text{CO})$  frequencies. In general, the predicted  $\nu(\text{PF})$  frequencies are found to be almost consistently lower than the experimental  $\nu(\text{PF})$  frequencies, typically by  $40 \pm 20 \text{ cm}^{-1}$ .

**Dissociation energies:** Table 7 lists dissociation energies for three reactions of particular interest in the chemistry of these iron trifluorophosphane complexes. The energy for dissociation of trifluorophosphane from  $[\text{Fe}(\text{PF}_3)_5]$  (**II**) to give singlet  $[\text{Fe}(\text{PF}_3)_4]$  (**IC**) is 33.6  $\text{kcal mol}^{-1}$  (B3LYP) or 41.8  $\text{kcal mol}^{-1}$  (BP86), which is comparable to the reported<sup>[58]</sup> CO dissociation energy of  $41 \pm 2 \text{ kcal mol}^{-1}$  for  $[\text{Fe}(\text{CO})_5]$ . The energy for dissociation of trifluorophosphane from  $[\text{Fe}_2(\text{PF}_3)_9]$  to give  $[\text{Fe}_2(\text{PF}_3)_8]$  is significantly less at 17.4  $\text{kcal mol}^{-1}$  (B3LYP) or 10.0  $\text{kcal mol}^{-1}$  (BP86). The energy for dissociation of  $\text{H}_2$  from  $[\text{H}_2\text{Fe}(\text{PF}_3)_4]$  (**IIIa**) to give singlet  $[\text{Fe}(\text{PF}_3)_4]$  (**IC**), namely 41.6  $\text{kcal mol}^{-1}$  (B3LYP) or 45.7  $\text{kcal mol}^{-1}$  (BP86), is roughly comparable.

The homolytic dissociation energy of  $[\text{Fe}_2(\text{PF}_3)_9]$  to two  $[\text{Fe}(\text{PF}_3)_4]$  fragments at 16.4  $\text{kcal mol}^{-1}$  (B3LYP) or 32.7  $\text{kcal mol}^{-1}$  (BP86) indicates that this species, for which we have postulated a formal  $\text{Fe}=\text{Fe}$  double bond, is high enough to indicate stability of this dimer towards dissociation. However, the dissociation of  $[\text{Fe}_2(\text{PF}_3)_9]$  (**VIa**) into the mononuclear fragments  $[\text{Fe}(\text{PF}_3)_5]$  (**II**) and singlet  $[\text{Fe}(\text{PF}_3)_4]$  (**IC**) is essentially thermoneutral within  $\approx 1 \text{ kcal mol}^{-1}$  suggesting thermodynamic instability of  $[\text{Fe}_2(\text{PF}_3)_9]$  relative to its mononuclear fragments.

## Discussion

The lowest energy structure for  $[\text{Fe}_2(\text{PF}_3)_9]$  (**VIa** in Figure 8) does not have any bridging intact  $\text{PF}_3$  groups analogous to the bridging carbonyl groups in  $[\text{Fe}_2(\text{CO})_9]$ , which has three bridging carbonyl groups, or  $[\text{Os}_2(\text{CO})_9]$ , which has a single bridging carbonyl group. Instead one of the  $\text{PF}_3$  ligands interacts with an iron atom to split a  $\text{P–F}$  bond forming a new  $\text{F}\rightarrow\text{Fe}$  bond and a  $\text{PF}_2$  group. This can be regarded as a rather unusual oxidative addition reaction since the formal oxidation state of the relevant iron atom increases from 0 to +2. The resulting  $[(\text{F}_3\text{P})_4\text{Fe}(\text{F})\text{PF}_2]$  unit, which has an octahedrally coordinated  $d^6 \text{ Fe}^{\text{II}}$ , can be regarded as a Lewis base, which coordinates to the  $[\text{Fe}(\text{PF}_3)_4]$  unit. Thus in **VIa** one of the iron atoms (the one with the  $\text{Fe–F}$  bond) is formally  $\text{Fe}^{\text{II}}$  and the other iron atom is formally  $\text{Fe}^0$ .

A second much higher energy structure (**VIb** in Figure 8) is found for  $[\text{Fe}_2(\text{PF}_3)_9]$  with an intact bridging  $\text{PF}_3$  group, and having a distorted trigonal bipyramidal phosphorus atom. However, unlike the related  $[\text{Os}_2(\text{CO})_9]$  (or  $[\text{Os}_2(\text{CO})_8(\mu\text{-CO})]$ ) with a single bridging carbonyl group,<sup>[59,60]</sup> the iron atoms in **VIb** are too far apart ( $\approx 4 \text{ Å}$ ) for the formal iron-iron single bond required to give both iron atoms the favored 18-electron configuration.

Table 6. Infrared  $\nu(\text{P-F})$  frequencies calculated using the BP86 method (calculated infrared intensities are given in parentheses in  $\text{kmol}^{-1}$ ; for the experimental infrared intensities vs. s, m, w, refer qualitatively to very strong, strong, medium, and weak, respectively).

Structures	$\nu(\text{P-F})$ [ $\text{cm}^{-1}$ ]
[Fe(PF <sub>3</sub> ) <sub>4</sub> ] ( <b>Ia</b> )	798(374), 800(385), 802(266), 816(60), 821(4), 828(220), 837(55), 843(0), 847(498), 849(450), 856(478), 893(47)
[Fe(PF <sub>3</sub> ) <sub>4</sub> ] ( <b>Ib</b> )	797(458), 798(354), 802(267), 817((39), 819(0), 824(41), 835(39), 841(476), 849(0), 849(494), 854(610), 893(45)
[Fe(PF <sub>3</sub> ) <sub>4</sub> ] ( <b>Ic</b> )	800(344), 801(182), 806(338), 812(90), 815(0), 825(237), 825(78), 845(584), 847(229), 854(0), 863(687), 901(35)
[Fe(PF <sub>3</sub> ) <sub>5</sub> ] ( <b>II</b> )	801(413), 801(413), 803(0), 816(117), 819(0), 819(0), 819(0), 826(91), 826(91), 852(1043), 870(0), 870(0), 872(633), 872(633), 911(0)
[Fe(PF <sub>3</sub> ) <sub>5</sub> ] exptl <sup>[26]</sup>	851(vs), 864(w), 901(vs), 915(vs)
[H <sub>2</sub> Fe(PF <sub>3</sub> ) <sub>4</sub> ] ( <b>IIIa</b> )	817(242), 824(367), 827(0), 836(0), 838(85), 849(242), 856(0), 857(66), 862(664), 869(530), 872(533), 903(2)
[H <sub>2</sub> Fe(PF <sub>3</sub> ) <sub>4</sub> ] ( <b>IIIb</b> )	813(82), 823(400), 823(400), 836(0), 838(0), 839(127), 839(127), 864(590), 865(0), 868(589), 868(589), 903(0)
[H <sub>2</sub> Fe(PF <sub>3</sub> ) <sub>4</sub> ] exptl <sup>[27]</sup>	871(vs), 864(w), 901(m), 918(vs), 939(w), 959(w)
[Fe <sub>2</sub> (PF <sub>3</sub> ) <sub>8</sub> ] ( <b>IVa</b> )	785(11), 790(36), 798(0), 799(12), 799(71), 801(279), 801(85), 807(347), 811(6), 813(0), 820(29), 823(22), 825(114), 828(965), 828(0), 845(120), 846(148), 853(0), 857(965), 864(69), 867(979), 872(994), 875(0), 909(0)
[Fe <sub>2</sub> (PF <sub>3</sub> ) <sub>8</sub> ] ( <b>IVb</b> )	540(0) <sup>[a]</sup> , 584(437) <sup>[a]</sup> , 801(450), 803(0), 803(0), 804(0), 809(91), 810(255), 814(192), 815(0), 818(0), 821(92), 823(0), 837(524), 840(600), 845(0), 854(0), 858(0), 859(35), 862(710), 867(921), 878(0), 880(1045), 907(0)
[Fe <sub>2</sub> (PF <sub>2</sub> ) <sub>2</sub> (PF <sub>3</sub> ) <sub>6</sub> ] ( <b>V</b> )	523(9) <sup>[a]</sup> , 546(119) <sup>[a]</sup> , 747(150), 748(13), 786(33), 801(132), 801(18), 808(406), 810(157), 815(5), 821(108), 831(430), 833(17), 842(122), 844(336), 850(927), 855(67), 862(5), 869(669), 870(220), 886(340), 893(92)
[Fe <sub>2</sub> (PF <sub>2</sub> ) <sub>2</sub> (PF <sub>3</sub> ) <sub>6</sub> ] exptl <sup>[10]</sup>	857(m), 870 (m), 890(w,sh), 909(m,sh), 922(s), 927 (s)
[Fe <sub>2</sub> (PF <sub>3</sub> ) <sub>9</sub> ] ( <b>VIa</b> )	738(46), 745(17), 796(308), 799(159), 810(27), 812(8), 814(248), 817(12), 820(307), 830(27), 842(270), 847(351), 852(35), 856(441), 856(189), 861(400), 862(21), 867(980), 875(785), 876(172), 881(86), 905(0), 907(468), 911(126)
[Fe <sub>2</sub> (PF <sub>3</sub> ) <sub>9</sub> ] ( <b>VIb</b> )	515(180) <sup>[a]</sup> , 744(37), 794(92), 801(49), 803(160), 808(58), 809(304), 815(312), 822(129), 824(13), 826(143), 834(93), 839(506), 843(54), 845(210), 849(1288), 850(145), 851(48), 857(87), 865(123), 874(179), 878(298), 890(829), 893(512), 902(44), 907(30)

[a] Bridging  $\nu(\text{P-F}\cdots\text{Fe})$  frequency.Table 7. Dissociation energies (in  $\text{kcal mol}^{-1}$ ) with and without zero-point energy corrections, and the entropy change (in  $\text{cal mol}^{-1} \text{K}$ ) for dissociation reactions.

	$\Delta E$		$\Delta E_{\text{ZPVE}}$		$\Delta S$	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
[Fe(PF <sub>3</sub> ) <sub>5</sub> ] ( <b>II</b> ) → [Fe(PF <sub>3</sub> ) <sub>4</sub> ] ( <b>Ic</b> ) + PF <sub>3</sub>	33.6	41.8	31.6	39.7	44.5	50.0
[Fe <sub>2</sub> (PF <sub>3</sub> ) <sub>9</sub> ] ( <b>VIa</b> ) → [Fe <sub>2</sub> (PF <sub>3</sub> ) <sub>8</sub> ] ( <b>IVa</b> ) + PF <sub>3</sub>	17.4	10.0	16.5	8.8	40.2	47.3
[H <sub>2</sub> Fe(PF <sub>3</sub> ) <sub>4</sub> ] ( <b>IIIa</b> ) → [Fe(PF <sub>3</sub> ) <sub>4</sub> ] ( <b>Ic</b> ) + H <sub>2</sub>	41.6	45.7	37.3	41.5	45.7	38.2
[Fe <sub>2</sub> (PF <sub>3</sub> ) <sub>8</sub> ] ( <b>IVa</b> ) → 2[Fe(PF <sub>3</sub> ) <sub>4</sub> ] ( <b>Ic</b> )	16.4	32.7	14.7	31.2	66.8	63.2
[Fe <sub>2</sub> (PF <sub>3</sub> ) <sub>9</sub> ] ( <b>VIa</b> ) → [Fe(PF <sub>3</sub> ) <sub>5</sub> ] ( <b>II</b> ) + [Fe(PF <sub>3</sub> ) <sub>4</sub> ] ( <b>Ic</b> )	0.1	0.9	-0.4	0.3	62.5	60.5

The dissociation energies summarized in Table 7 predict [Fe<sub>2</sub>(PF<sub>3</sub>)<sub>9</sub>] to be a relatively unstable species, at least from a thermodynamic point of view. Thus the dissociation energy for loss of one PF<sub>3</sub> ligand from [Fe<sub>2</sub>(PF<sub>3</sub>)<sub>9</sub>] to give [Fe<sub>2</sub>(PF<sub>3</sub>)<sub>8</sub>] is much smaller than that from [Fe(PF<sub>3</sub>)<sub>5</sub>] to give [Fe(PF<sub>3</sub>)<sub>4</sub>]. More significantly, the dissociation of [Fe<sub>2</sub>(PF<sub>3</sub>)<sub>9</sub>] to give [Fe(PF<sub>3</sub>)<sub>5</sub>] + [Fe(PF<sub>3</sub>)<sub>4</sub>] is essentially thermoneutral.

The coordinatively unsaturated binuclear [Fe<sub>2</sub>(PF<sub>3</sub>)<sub>8</sub>] was found to have an unbridged structure with two [Fe(PF<sub>3</sub>)<sub>4</sub>] units linked solely by an iron-iron bond (**IVa** in Figure 5). The  $\approx 2.5 \text{ \AA}$  length of this Fe=Fe bond is consistent with the formal double bond required to give both iron atoms the favored 18-electron configuration. This dimer is stable thermodynamically with respect to dissociation into two mononuclear [Fe(PF<sub>3</sub>)<sub>4</sub>] units unlike [Fe<sub>2</sub>(PF<sub>3</sub>)<sub>9</sub>] (Table 7).

We also studied the binuclear derivative [Fe<sub>2</sub>(PF<sub>3</sub>)<sub>6</sub>(PF<sub>2</sub>)<sub>2</sub>], expected to have two bridging PF<sub>2</sub> groups. Such a structure (**V** in Figure 6) was indeed found. However, the bridging PF<sub>2</sub> groups are an unusual kind, which bond to only one iron atom through the phosphorus atom and to the other iron atom through one of the fluorine atoms. An uncomplexed lone pair remains on the PF<sub>2</sub> phosphorus atom in the case of this unusual PF<sub>2</sub> group. This unusual type of bridging PF<sub>2</sub> group is different from the typical bridging PX<sub>2</sub> group

in [Fe<sub>2</sub>L<sub>6</sub>( $\mu$ -PX<sub>2</sub>)<sub>2</sub>] derivatives (L = most commonly CO), where the PX<sub>2</sub> phosphorus atom is bonded to both iron atoms and the X groups remain as "innocent bystanders".

The mononuclear derivatives [Fe(PF<sub>3</sub>)<sub>4</sub>], [Fe(PF<sub>3</sub>)<sub>5</sub>], and [H<sub>2</sub>Fe(PF<sub>3</sub>)<sub>4</sub>] were also investigated during the course of this

work. The lowest energy structures of [Fe(PF<sub>3</sub>)<sub>4</sub>] were found to be triplet electronic states displaying tetrahedral FeP<sub>4</sub> coordination, with the two rotamers **Ia** and **Ib** (Figure 2) within 1.2  $\text{kcal mol}^{-1}$  energetically of each other. These rotamers differ only in rotation about the Fe-P bonds, leading to different relative orientations of the PF<sub>3</sub> ligands with no significant change in the FeP<sub>4</sub> coordination. Clearly, similar rotamers are not possible for the corresponding [Fe(CO)<sub>4</sub>] derivatives. The iron atom in these triplet structures of [Fe(PF<sub>3</sub>)<sub>4</sub>] uses all nine orbitals of its  $\text{sp}^3\text{d}^5$  manifold, but two of these orbitals are only singly occupied, leading to the triplet spin multiplicity. The corresponding singlet structure of [Fe(PF<sub>3</sub>)<sub>4</sub>], namely **Ic** (Figure 2), was also found, but at a significantly higher energy (Table 1).

The tetrahedral structures for [Fe(PF<sub>3</sub>)<sub>4</sub>] are very different from those of the carbonyl analogues. Thus a  $C_{2v}$  structure was suggested for triplet [Fe(CO)<sub>4</sub>] from a detailed study of its infrared  $\nu(\text{CO})$  frequencies in solid matrices and using time-resolved infrared spectroscopy in the gas phase.<sup>[61]</sup> This  $C_{2v}$  structure proposed for triplet [Fe(CO)<sub>4</sub>] is derived from a trigonal bipyramid by removing an axial CO group and thus has lower local coordination symmetry around the iron atom. A similar  $C_{2v}$  structure was suggested for the singlet transient [Fe(CO)<sub>4</sub>] generated by the photolysis of

[Fe(CO)<sub>5</sub>] and detected using ultrafast electron diffraction.<sup>[62,63]</sup> These differences between the analogous [Fe-(PF<sub>3</sub>)<sub>4</sub>] and [Fe(CO)<sub>4</sub>] may arise from the significantly greater steric demands of the PF<sub>3</sub> ligand. These demands can best be accommodated by distributing the PF<sub>3</sub> ligands in [Fe-(PF<sub>3</sub>)<sub>4</sub>] as far apart as possible, corresponding to the vertices of a tetrahedron rather than those of the less symmetrical C<sub>2v</sub> polyhedron found in [Fe(CO)<sub>4</sub>].

The situation with the saturated [Fe(PF<sub>3</sub>)<sub>5</sub>] is relatively simple, since only one structure **II** was found at reasonable energies. This structure is the expected trigonal bipyramid, which is analogous to the well established trigonal bipyramid structure for the analogous [Fe(CO)<sub>5</sub>].

Both *cis* and *trans* isomers were found for the dihydride [H<sub>2</sub>Fe(PF<sub>3</sub>)<sub>4</sub>] with the *cis* isomer **IIIa** being of significantly lower energy than the *trans* isomer. The iron coordination in the *cis* isomer appears to be nearly perfectly octahedral whereas in the *trans* isomer the FeP<sub>4</sub> coordination subunit is distorted towards tetrahedral. Thus the six-coordinate FeP<sub>4</sub>H<sub>2</sub> unit in *trans*-[H<sub>2</sub>Fe(PF<sub>3</sub>)<sub>4</sub>] approaches that of a C<sub>2v</sub> bicapped tetrahedron.

## Conclusion

This work demonstrates for the first time in a concrete manner some major differences between the PF<sub>3</sub> and CO ligands in low-valent transition metal chemistry, particularly with respect to an unanticipated role of the fluorine atoms in the metal-ligand bonding. Thus, in binuclear metal trifluorophosphane complexes the fluorine atoms of the PF<sub>3</sub> ligands as well as the phosphorus atoms are involved in the metal-ligand bonding as indicated by the lowest energy structure **VIa** of [Fe<sub>2</sub>(PF<sub>3</sub>)<sub>9</sub>]. Even in the case of the bridging PF<sub>2</sub> group in [Fe<sub>2</sub>(PF<sub>3</sub>)<sub>6</sub>(PF<sub>2</sub>)<sub>2</sub>], a fluorine lone pair is used in preference to the phosphorus lone pair.

## Acknowledgements

We are indebted to the 111 Project (B07012) in China and the U.S. National Science Foundation (Grants CHE-0749868 and CHE-0716718) for support of this research.

- [1] J. F. Nixon, *Adv. Inorg. Chem.* **1985**, 29, 41.
- [2] L. Mond, C. Langer, F. Quincke, *J. Chem. Soc.* **1890**, 57, 749.
- [3] J. W. Irvine, G. Wilkinson, *Science* **1951**, 113, 742.
- [4] J. W. Irvine, G. Wilkinson, *J. Am. Chem. Soc.* **1951**, 73, 5501.
- [5] T. Kruck, *Angew. Chem.* **1967**, 79, 27; *Angew. Chem. Int. Ed. Engl.* **1967**, 6, 53.
- [6] T. Kruck, *Z. Naturf.* **1964**, 19, 164.
- [7] T. Kruck, K. Baur, *Angew. Chem.* **1965**, 77, 505.
- [8] T. Kruck, K. Baur, *Z. Anorg. Allg. Chem.* **1969**, 364, 192.
- [9] P. L. Timms, *J. Chem. Soc. D* **1969**, 1033.
- [10] P. L. Timms, *J. Chem. Soc. A* **1970**, 2526.
- [11] R. J. Clark, *Inorg. Chem.* **1964**, 3, 1395.
- [12] J. C. Green, D. I. King, J. H. D. Eland, *J. Chem. Soc. D* **1970**, 1121.
- [13] I. H. Hiller, V. R. Saunders, M. J. Ware, P. J. Bassett, D. R. Lloyd, N. Lynam, *J. Chem. Soc. D* **1970**, 1316.

- [14] P. J. Bassett, B. R. Higginson, D. R. Lloyd, N. Lynam, P. J. Roberts, *J. Chem. Soc. Dalton* **1974**, 2316.
- [15] J. Müller, K. Fenderl, B. Mertschen, *Chem. Ber.* **1971**, 104, 700.
- [16] R. A. Head, J. F. Nixon, G. J. Sharp, R. J. Clark, *J. Chem. Soc. Dalton* **1975**, 2054.
- [17] J. F. Nixon, E. A. Seddon, R. J. Suffolk, M. J. Taylor, J. C. Green, R. J. Clark, *J. Chem. Soc. Dalton* **1986**, 765.
- [18] J.-M. Savariault, A. Serafini, M. Pellissier, P. Cassoux, *Theor. Chim. Acta* **1976**, 42, 155.
- [19] M. Braga, *Inorg. Chem.* **1985**, 24, 2702.
- [20] M. Braga, *J. Mol. Struct. THEOCHEM* **1992**, 85, 167.
- [21] G. Frenking, K. Wichmann, N. Fröhlich, J. Grobe, W. Golla, D. Le Van, B. Krebs, M. Läge, *Organometallics*, **2002**, 21, 2921.
- [22] M. A. Bennett, R. N. Johnson, T. W. Turney, *Inorg. Chem.* **1976**, 15, 2938.
- [23] T. Drews, D. Rusch, S. Seidel, S. Willemsen, K. Seppelt, *Chem. Eur. J.* **2008**, 14, 4280.
- [24] C. L. Hammill, R. J. Clark, C. W. Ross, A. G. Marshall, J. Schmutz, *Inorg. Chem.* **1997**, 36, 5973.
- [25] T. Kruck, A. Prash, *Angew. Chem.* **1964**, 76, 892.
- [26] T. Kruck, A. Prash, *Z. Anorg. Allg. Chem.* **1968**, 356, 118.
- [27] T. Kruck, A. Prash, *Z. Anorg. Allg. Chem.* **1969**, 371, 1.
- [28] T. Kruck, R. Kobelt, *Chem. Ber.* **1972**, 105, 3765.
- [29] T. Kruck, R. Kobelt, *Chem. Ber.* **1972**, 105, 3772.
- [30] H. M. Powell, R. V. G. Ewens, *J. Chem. Soc.* **1939**, 286.
- [31] F. A. Cotton, J. M. Troup, *J. Chem. Soc. Dalton* **1974**, 800.
- [32] A. W. Ehlers, G. Frenking, *J. Am. Chem. Soc.* **1994**, 116, 1514.
- [33] B. Delley, M. Wrinn, H. P. Lüthi, *J. Chem. Phys.* **1994**, 100, 5785.
- [34] J. Li, G. Schreckenbach, T. Ziegler, *J. Am. Chem. Soc.* **1995**, 117, 486.
- [35] V. Jonas, W. Thiel, *J. Chem. Phys.* **1995**, 102, 8474.
- [36] T. A. Barckholtz, B. E. Bursten, *J. Am. Chem. Soc.* **1998**, 120, 1926.
- [37] S. Niu, M. B. Hall, *Chem. Rev.* **2000**, 100, 353.
- [38] P. Macchi, A. Sironi, *Coord. Chem. Rev.* **2003**, 238, 383.
- [39] J.-L. Carreon, J. N. Harvey, *Phys. Chem. Chem. Phys.* **2006**, 8, 93.
- [40] M. Bühl, H. Kabrede, *J. Chem. Theory Comput.* **2006**, 2, 1282.
- [41] A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648.
- [42] C. Lee, W. Yang, R. G. Parr, *Rev. Phys. B* **1988**, 37, 785.
- [43] A. D. Becke, *Rev. Phys. A* **1988**, 38, 3098.
- [44] J. P. Perdew, *Rev. Phys. B* **1986**, 33, 8822.
- [45] See especially F. Furche, J. P. Perdew, *J. Chem. Phys.* **2006**, 124, 044103.
- [46] H. Y. Wang, Y. Xie, R. B. King, H. F. Schaefer, *J. Am. Chem. Soc.* **2005**, 127, 11646.
- [47] H. Y. Wang, Y. Xie, R. B. King, H. F. Schaefer, *J. Am. Chem. Soc.* **2006**, 128, 11376.
- [48] T. H. Dunning, *J. Chem. Phys.* **1970**, 53, 2823.
- [49] S. Huzinaga, *J. Chem. Phys.* **1965**, 42, 1293.
- [50] T. H. Dunning, P. Hay in *Modern Theoretical Chemistry*, vol 3 (Ed.: H. F. Schaefer), **1977**, Plenum Press, New York.
- [51] A. J. H. Wächters, *J. Chem. Phys.* **1970**, 52, 1033.
- [52] D. M. Hood, R. M. Pitzer, H. F. Schaefer, *J. Chem. Phys.* **1979**, 71, 705.
- [53] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W.



- Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian Inc, Gaussian, Wallingford CT, **2004**.
- [54] B. N. Papas, H. F. Schaefer, *J. Mol. Struct.* **2006**, 768, 175.
- [55] H. Jacobsen, T. Ziegler, *J. Am. Chem. Soc.* **1996**, 118, 4631.
- [56] J. M. L. Martin, C. W. Bauschlicher, A. Ricca, *Comput. Phys. Commun.* **2001**, 133, 189.
- [57] T. Kruck, W. Lang, *Angew. Chem.* **1967**, 79, 474; *Angew. Chem. Int. Ed. Engl.* **1967**, 6, 454.
- [58] A. W. Ehlers, G. Frenking, *Organometallics* **1995**, 14, 423.
- [59] J. R. Moss, W. A. G. Graham, *J. Chem. Soc. D* **1970**, 835.
- [60] J. R. Moss, W. A. G. Graham, *J. Chem. Soc. Dalton Trans.* **1977**, 95.
- [61] M. Poliakoff, E. Weitz, *Acc. Chem. Res.* **1987**, 20, 408.
- [62] H. Ihee, J. Cao, A. H. Zewail, *Angew. Chem.* **2001**, 113, 1580; *Angew. Chem. Int. Ed.* **2001**, 40, 1532.
- [63] M. Poliakoff, J. J. Turner, *Angew. Chem.* **2001**, 113, 2889; *Angew. Chem. Int. Ed.* **2001**, 40, 2809.

Received: June 24, 2008

Published online: October 27, 2008