

*Dedicated to Professor Luminița Silaghi-Dumitrescu  
on the occasion of her 65<sup>th</sup> anniversary*

## THE QUEST FOR BRIDGING TRIFLUOROPHOSPHINE LIGANDS IN TRANSITION METAL COMPLEXES

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**ABSTRACT.** Trifluorophosphine is a strong back-bonding ligand like the ubiquitous carbonyl ligand. In fact mononuclear zerovalent trifluorophosphine complexes such as  $M(PF_3)_6$  ( $M = Cr, Mo, W$ ),  $M(PF_3)_5$  ( $M = Fe, Ru$ ), and  $M(PF_3)_4$  ( $M = Ni, Pt$ ) are even more stable than their well-known carbonyl analogues. However, metal complexes with bridging trifluorophosphine ligands are virtually unknown. We review theoretical studies on the  $Co_2(PF_3)_8$ ,  $Fe_2(PF_3)_9$ , and  $Cp_2Fe_2(PF_3)_n$  ( $Cp = \eta^5-C_5H_5$ ;  $n = 4, 3$ ) systems analogous to the well-known metal carbonyls  $Co_2(CO)_6(\mu-CO)_2$ ,  $Fe_2(CO)_6(\mu-CO)_3$ ,  $Cp_2Fe_2(CO)_2(\mu-CO)_2$ , and  $Cp_2Fe_2(\mu-CO)_3$  containing two or three bridging CO groups. In most cases structures having features other than bridging  $PF_3$  groups are energetically preferred.

**Keywords:** Trifluorophosphine, iron, cobalt, density functional theory

### INTRODUCTION

The use of carbon monoxide as a ligand to stabilize low transition metal oxidation states dates back to the discovery of nickel tetracarbonyl in 1890 as a volatile liquid containing formally zerovalent nickel [1]. Other transition metals were subsequently found to form similar zerovalent binary metal carbonyls as exemplified by  $Cr(CO)_6$ ,  $Mn_2(CO)_{10}$ ,  $Fe(CO)_5$ , and  $Co_2(CO)_8$ . A key to the stabilization of formally zerovalent transition metal derivatives is the removal of electron density from the metal atom by  $d\pi \rightarrow p\pi^*$  back-donation from filled metal d orbitals into empty CO  $\pi^*$  antibonding orbitals.

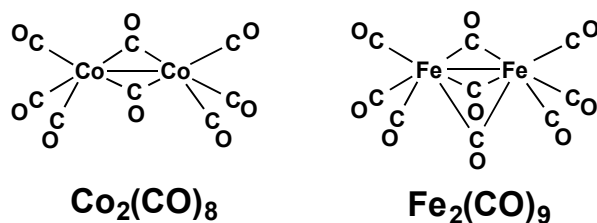
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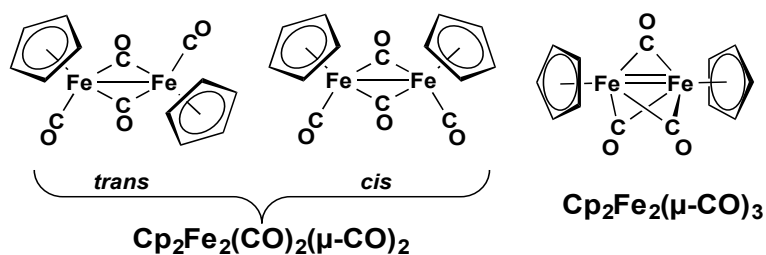
The unusual properties of the CO ligand in stabilizing low oxidation states stimulated the search for other ligands with similar properties. In this connection Wilkinson and Irvine [2] in 1951 discovered the binary zerovalent nickel trifluorophosphine complex  $\text{Ni}(\text{PF}_3)_4$ , as a volatile liquid considerably more stable than  $\text{Ni}(\text{CO})_4$ . Subsequent work led to the extensive development of metal trifluorophosphine chemistry, particularly in the laboratories of Kruck et al. Thus reactions of phosphorus trifluoride under pressure with various transition metal derivatives led to a variety of metal very stable trifluorophosphine complexes [3, 4, 5, 6, 7, 8, 9, 10, 11, 12]. The strong back-bonding of the trifluorophosphine ligand in metal trifluorophosphine complexes can be related to the the electron withdrawing properties of its three highly electronegative fluorine atoms [13, 14, 15, 16, 17, 18, 19, 20, 21, 22]. Thus  $\text{PF}_3$  ligands, like CO ligands, stabilize low formal oxidation states so that zerovalent metal derivatives, such as  $\text{Cr}(\text{PF}_3)_6$ ,  $\text{Fe}(\text{PF}_3)_5$ , and  $\text{Ni}(\text{PF}_3)_4$ , are essentially stable towards air oxidation. In addition, their volatility is comparable to the analogous metal carbonyls despite their considerably higher molecular weights. In addition several binary zerovalent metal trifluorophosphine complexes without currently known stable homoleptic metal carbonyl counterparts are known including  $\text{M}_2(\text{PF}_3)_8$  (M = Rh, Ir) [23],  $\text{Pt}(\text{PF}_3)_4$  [24, 25, 26] and  $\text{Pt}_4(\text{PF}_3)_8$  [27]. This suggests that  $\text{PF}_3$  is even better than CO in stabilizing low transition metal oxidation states. In addition to the strong back-donation of  $\text{PF}_3$  ligands, the greater steric protection of the central metal atom by multiple  $\text{PF}_3$  ligands relative to that by multiple CO ligands may enhance the stability of some zerovalent metal trifluorophosphine complexes.

These observations on the higher stability of metal trifluorophosphine complexes relative to corresponding metal carbonyls suggested originally that metal trifluorophosphine chemistry might evolve into a more extensive area of inorganic chemistry than even metal carbonyl chemistry. However, as metal trifluorophosphine chemistry continued to develop, metal trifluorophosphine complexes with bridging  $\text{PF}_3$  groups analogous to well-known metal carbonyls with bridging carbonyl groups (Figure 1) such as  $\text{Co}_2(\text{CO})_8$  { =  $\text{Co}_2(\text{CO})_6(\mu\text{-CO})_2$  } [28, 29, 30, 31] and  $\text{Fe}_2(\text{CO})_9$  { =  $\text{Fe}_2(\text{CO})_6(\mu\text{-CO})_3$  } [32, 33] remained unknown even though metal trifluorophosphine complexes with terminal  $\text{PF}_3$  groups are generally more stable than their carbonyl counterparts.



**Figure 1.** The bridged structures of  $\text{Co}_2(\text{CO})_8$  and  $\text{Fe}_2(\text{CO})_9$ .

The cyclopentadienyliron carbonyl  $\text{Cp}_2\text{Fe}_2(\text{CO})_4$  is another example of a common metal carbonyl derivative containing two bridging CO groups. In fact, *cis* and *trans* isomers of  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$  can be isolated separately and structurally characterized by X-ray crystallography (Figure 2) [34, 35, 36]. The doubly bridged Fe–Fe bonding distances in these structures are  $\sim 2.54$  Å corresponding to formal single bonds. Again the analogous  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_2(\mu\text{-PF}_3)_2$  with two bridging  $\text{PF}_3$  groups remains unknown even though related CpFe species with terminal  $\text{PF}_3$  groups such as  $\text{CpFe}(\text{PF}_3)_2\text{H}$  have been synthesized [37]. Another stable binuclear cyclopentadienyliron carbonyl is the triply bridged  $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_3$ , which can be synthesized by photolysis of  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$  at low temperatures. This species is of interest in being a stable organometallic triplet state molecule [38, 39, 40, 41]. Thus, the Fe=Fe formal double bond of length 2.265 Å in  $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_3$  has two orthogonal single-electron orthogonal  $\pi$  “half-bond” components analogous to the O=O double bond in ordinary dioxygen thereby accounting for the triplet spin state of this molecule. An analogous  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_3$  has not been synthesized.



**Figure 2.** The *trans* and *cis* isomers of the doubly bridged  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$  [=  $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ ] and the triply bridged  $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_3$  structure.

In order to gain some insight into the reasons for the lack of binuclear transition metal complexes having bridging  $\text{PF}_3$  groups, we undertook a density functional theory study of trifluorophosphine analogues of binuclear metal carbonyls with bridging CO groups. We review here the highlights of our studies on the  $\text{Co}_2(\text{PF}_3)_8$  [42],  $\text{Fe}_2(\text{PF}_3)_9$  [43], and  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_n$  ( $n = 4, 3$ ) [44] systems analogous to  $\text{Co}_2(\text{CO})_8$ ,  $\text{Fe}_2(\text{CO})_9$ , and  $\text{Cp}_2\text{Fe}_2(\text{CO})_n$ , respectively. Further details are provided in the individual cited articles.

## RESULTS AND DISCUSSION

Optimization of  $\text{Co}_2(\text{PF}_3)_8$  led only to the unbridged structure having a predicted Co–Co distance of  $\sim 2.77$  Å (Figure 3). This Co–Co distance is somewhat longer than the experimental Co–Co distance of  $\sim 2.70$  Å in an

analogous unbridged  $(\text{OC})_4\text{Co}-\text{Co}(\text{CO})_4$  isomer stabilized in a  $\text{C}_{60}$  matrix [45]. The lengthening of the unbridged  $\text{Co}-\text{Co}$  bond upon substituting all of the  $\text{CO}$  groups with  $\text{PF}_3$  groups may be a consequence of the greater steric bulk of  $\text{PF}_3$ , thereby forcing the cobalt atoms to remain at a longer distance from each other. The doubly bridged  $\text{Co}_2(\text{CO})_6(\mu\text{-CO})_2$  isomer has a shorter  $\text{Co}-\text{Co}$  distance of  $\sim 2.53$  Å owing to a bond-shortening effect of the two bridging  $\text{CO}$  groups [46, 47, 48]. The bridged  $\text{Co}_2(\text{CO})_6(\mu\text{-CO})_2$  and unbridged  $\text{Co}_2(\text{CO})_8$  isomers are shown to be in equilibrium in solution [49, 50, 51, 52, 53] and are calculated by density functional theory to have similar energies.

A bridging  $\text{PF}_3$  group is a feature of the only  $\text{Co}_2(\text{PF}_3)_9$  structure found in the density functional theory study (Figure 3). This structure may be regarded as a substitution product of  $\text{PF}_5$  in which the two axial fluorine atoms have been replaced by  $-\text{Co}(\text{PF}_3)_4$  units, i. e., one-half of the optimized  $\text{Co}_2(\text{PF}_3)_8$  structure. However,  $\text{Co}_2(\text{PF}_3)_9$  appears to be disfavored thermochemically with respect to exothermic  $\text{PF}_3$  loss by  $\sim 10$  kcal/mol to give  $\text{Co}_2(\text{PF}_3)_8$ . Thus  $\text{Co}_2(\text{PF}_3)_9$  is not likely to be a viable species. A high-energy  $\text{Co}_2(\text{PF}_3)_7$  structure is also found with a bridging  $\text{PF}_3$  group between two  $\text{Co}(\text{PF}_3)_3$  units without a  $\text{Co}-\text{Co}$  bond. However, this  $\text{Co}_2(\text{PF}_3)_6(\mu\text{-PF}_3)$  structure lies  $\sim 60$  kcal/mol in energy above the lowest energy  $\text{Co}_2(\text{PF}_3)_7$  structure and thus does not appear to be a viable species.

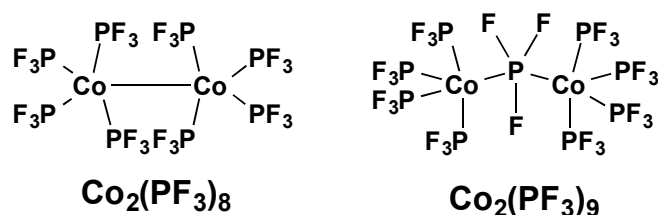
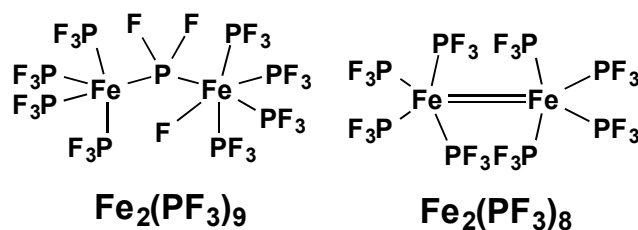


Figure 3. Structures of  $\text{Co}_2(\text{PF}_3)_n$  ( $n = 8, 9$ ).

The experimental  $\text{Fe}_2(\text{CO})_9$  structure is the triply bridged isomer  $\text{Fe}_2(\text{CO})_6(\mu\text{-CO})_3$  [54, 55]. However, a singly bridged  $\text{Fe}_2(\text{CO})_8(\mu\text{-CO})$  isomer is of comparable energy. An analogous singly bridged  $\text{Os}_2(\text{CO})_8(\mu\text{-CO})$  structure is the experimental  $\text{Os}_2(\text{CO})_9$  structure. The lowest energy  $\text{Fe}_2(\text{PF}_3)_9$  structure by  $\sim 28$  kcal/mol (Figure 4) is related to the lowest-energy  $\text{Co}_2(\text{PF}_3)_9$  structure (Figure 3) by migration of a fluorine atom from the bridging phosphorus atom to an iron atom leaving a bridging  $\text{PF}_2$  group rather than a bridging  $\text{PF}_3$  group. Formation of the  $\text{Fe}_2(\text{PF}_3)_8(\text{F})(\mu\text{-PF}_2)$  structure for  $\text{Fe}_2(\text{PF}_3)_9$  can also be interpreted as insertion of an iron atom into a  $\text{P}-\text{F}$  bond of an initially bridging  $\text{PF}_3$  ligand. The driving force for the splitting of the neutral  $\text{PF}_3$  ligand into the anionic  $\text{PF}_2$  and  $\text{F}$  ligands can relate to the reducing power of zerovalent iron.

Similar bridging  $\text{PF}_2$  groups are found in the binuclear derivatives  $\text{M}_2(\text{PF}_3)_6(\mu\text{-PF}_2)_2$  ( $\text{M} = \text{Fe}, \text{Co}$  [56]). These observations suggest that bridging  $\text{PF}_2$  groups are more favorable than bridging  $\text{PF}_3$  groups.



**Figure 4.** Lowest energy structures of  $\text{Fe}_2(\text{PF}_3)_n$  ( $n = 8, 9$ )

The dissociation energy of  $\text{Fe}_2(\text{PF}_3)_9$  to give  $\text{Fe}_2(\text{PF}_3)_8 + \text{PF}_3$  is  $\sim 13$  kcal/mol, which is significantly lower than CO dissociation from the stable binary metal carbonyls. Thus the experimental CO dissociation energies of  $\text{Cr}(\text{CO})_6$ ,  $\text{Fe}(\text{CO})_5$ , and  $\text{Ni}(\text{CO})_4$  are 37, 41, and 27 kcal/mol, respectively [57]. More significantly, dissociation of  $\text{Fe}_2(\text{PF}_3)_9$  into the mononuclear fragments  $\text{Fe}(\text{PF}_3)_5 + \text{Fe}(\text{PF}_3)_4$  is essentially thermoneutral within  $\sim 1$  kcal/mol suggesting that  $\text{Fe}_2(\text{PF}_3)_9$  is not a viable species. However, the dissociation of  $\text{Fe}_2(\text{PF}_3)_8$  into two  $\text{Fe}(\text{PF}_3)_4$  fragments is clearly endothermic at  $\sim 25$  kcal/mol. The optimized  $\text{Fe}_2(\text{PF}_3)_8$  structure consists of two  $\text{Fe}(\text{PF}_3)_4$  units linked solely by an  $\text{Fe}=\text{Fe}$  bond of length  $\sim 2.51$  Å. This  $\text{Fe}=\text{Fe}$  distance is  $\sim 0.26$  Å shorter than the  $\text{Co}-\text{Co}$  single bond in the likewise unbridged  $\text{Co}_2(\text{PF}_3)_8$  structure (Figure 3). This supports the formulation of the  $\text{Fe}=\text{Fe}$  bond in  $\text{Fe}_2(\text{PF}_3)_8$  as the formal double bond needed to give each iron atom the favored 18-electron configuration. The carbonyl  $\text{Fe}_2(\text{CO})_8$  analogous to  $\text{Fe}_2(\text{PF}_3)_8$  has been detected spectroscopically in low-temperature matrices but is not viable not under normal conditions [58, 59, 60].

A density functional theory study on the  $\text{Cp}_2\text{Fe}_2(\text{CO})_4$  system shows the *cis* and *trans* isomers of the doubly bridged  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$  structure (Figure 2) to be the lowest energy structures consistent with the fact that both stereoisomers have been isolated and characterized structurally by X-ray crystallography. However, an unbridged  $\text{Cp}_2\text{Fe}_2(\text{CO})_4$  isomer was also found lying  $\sim 6$  kcal/mol in energy above the doubly bridged  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$  isomers. The predicted  $\text{Fe}-\text{Fe}$  distance of  $\sim 2.73$  Å in the unbridged  $\text{Cp}_2\text{Fe}_2(\text{CO})_4$  isomer is  $\sim 0.2$  Å longer than that in the doubly bridged  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$  isomer. A density functional theory study on the  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_4$  system using methods similar to those used earlier for the  $\text{Cp}_2\text{Fe}_2(\text{CO})_4$  system led to only unbridged *cis* and *trans* structures with no

evidence for any low-energy  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_4$  structures with bridging  $\text{PF}_3$  groups. The less sterically hindered *trans*- $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_4$  structure was found to lie  $\sim 5$  kcal/mol in energy below its *cis* stereoisomer. The predicted Fe–Fe distances of  $\sim 2.98$  Å and  $\sim 3.01$  Å for *trans*- and *cis*- $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_4$ , respectively, are nearly 0.3 Å longer than that for the unbridged  $\text{Cp}_2\text{Fe}_2(\text{CO})_4$  isomer. This presumably is an effect of the greater bulk of the  $\text{CpFe}(\text{PF}_3)_2$  halves of the  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_4$  molecule as compared with the  $\text{CpFe}(\text{CO})_2$  halves of the unbridged  $\text{Cp}_2\text{Fe}_2(\text{CO})_4$  molecule.

A density functional theory study on the  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_3$  system also showed the only structures within  $\sim 11$  kcal/mol of the lowest energy structure to be unbridged triplet and quintet spin state structures with two terminal  $\text{PF}_3$  groups on one iron atom and a third terminal  $\text{PF}_3$  group on the other iron atom. This is in stark contrast to the experimentally known triply bridged  $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_3$  structure of the carbonyl analogue. The Fe=Fe distances in these unbridged  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_3$  structures range from  $\sim 2.44$  Å for a quintet spin state structure to 2.7 to 2.8 Å for the triplet spin state structures. All of these Fe=Fe distances are significantly less than the  $\sim 3.0$  Å Fe–Fe single bond distances in the unbridged  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_4$  structures thereby suggesting formal double bonds of various types.

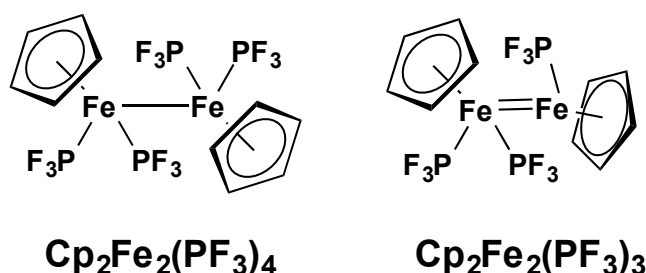
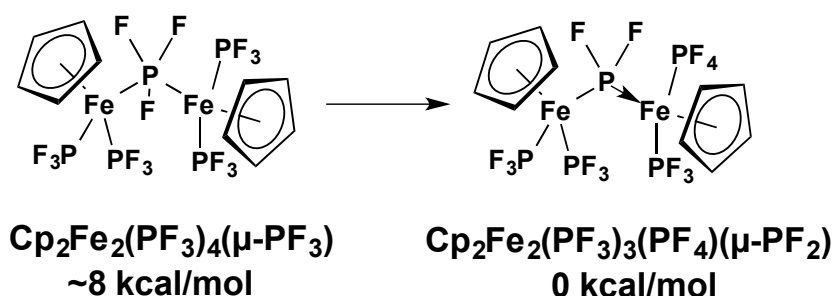


Figure 5. The lowest energy  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_n$  ( $n = 4, 3$ ) structures.

The pentacarbonyl  $\text{Cp}_2\text{Fe}_2(\text{CO})_5$  is not known and presumed not to be viable. Application of the 18-electron rule and assuming the nearly universal terminal pentahapto coordination of the Cp ligands require the absence of an iron-iron bond in  $\text{Cp}_2\text{Fe}_2(\text{CO})_5$ . This means that a bridging CO group is the only way to hold the two iron atoms together in  $\text{Cp}_2\text{Fe}_2(\text{CO})_5$ . However, the trifluorophosphine analogue  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_5$  appears to be viable since loss of  $\text{PF}_3$  to give  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_4$  is endothermic at  $\sim 23$  kcal/mol. Furthermore, a  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_4(\mu\text{-PF}_3)$  structure with a bridging  $\text{PF}_3$  group lies within  $\sim 8$  kcal/mol of the lowest energy  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_5$  isomer (Figure 6). However, the lowest energy  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_5$  structure has a bridging  $\mu\text{-PF}_2$  group and a terminal  $\text{PF}_4$  group, i. e.,  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_3(\text{PF}_4)(\mu\text{-PF}_2)$  in which a

fluorine atom has migrated from the bridging  $\text{PF}_3$  group to a terminal  $\text{PF}_3$  group. The predicted exothermicity of this process indicates that bridging  $\text{PF}_2$  groups with four-coordinate phosphorus atoms are more favorable than bridging  $\text{PF}_3$  groups with five-coordinate phosphorus atoms. The terminal  $\text{PF}_4$  group bonded to the iron atom is related to phosphorus pentafluoride by replacing one of the  $\text{P-F}$  bonds with a  $\text{P-Fe}$  bond. It is a net donor of one electron to the iron atom so both iron atoms in the  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_3(\text{PF}_4)(\mu\text{-PF}_2)$  structure have the favored 18-electron configuration.



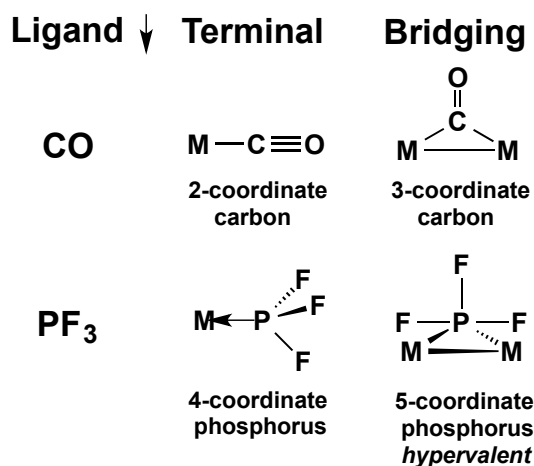
**Figure 6.** The exothermic conversion of  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_4(\mu\text{-PF}_3)$  to  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_3(\text{PF}_4)(\mu\text{-PF}_2)$  involving fluorine migration from a bridging  $\text{PF}_3$  group to a terminal  $\text{PF}_3$  group.

## CONCLUSIONS

Density functional theory studies on the  $\text{Co}_2(\text{PF}_3)_8$ ,  $\text{Fe}_2(\text{PF}_3)_9$ , and  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_n$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ;  $n = 4, 3$ ) systems confirm the experimentally observed reluctance for the strong back-bonding  $\text{PF}_3$  ligand to form binuclear metal complexes containing bridging  $\text{PF}_3$  groups despite the fact that their carbonyl analogues contain two or three  $\text{CO}$  groups bridging a central metal-metal bond. Thus for  $\text{Co}_2(\text{PF}_3)_8$  and  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_n$  ( $n = 4, 3$ ) all of the low-energy structures are unbridged structures with the two parts held together only by metal-metal bonds. The lowest energy  $\text{Fe}_2(\text{PF}_3)_9$  structure by a substantial margin is of the type  $\text{Fe}_2(\text{PF}_3)_8(\text{F})(\mu\text{-PF}_2)$  where one of the iron atoms has inserted into a  $\text{P-F}$  bond of one of the  $\text{PF}_3$  ligands.

Bridging  $\text{PF}_3$  groups without a central metal-metal bond are found in low-energy structures of the ligand-rich species  $\text{Co}_2(\text{PF}_3)_9$  and  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_5$ . However,  $\text{Co}_2(\text{PF}_3)_9$  is not likely to be a viable species since loss of one  $\text{PF}_3$  ligand to give  $\text{Co}_2(\text{PF}_3)_8$  is an exothermic process by  $\sim 10$  kcal/mol. Furthermore the  $\text{PF}_3$ -bridged  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_4(\mu\text{-PF}_3)$  is disfavored relative to migration of fluorine from the bridging  $\text{PF}_3$  group to a terminal  $\text{PF}_3$  group to give  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_3(\text{PF}_4)(\mu\text{-PF}_2)$ .

The reluctance of  $\text{PF}_3$  to bridge two metal atoms compared with CO can be related to the coordination number of the donor atom. Thus terminal and bridging CO groups have dicoordinate and tricoordinate carbon atoms, respectively (Figure 7). Similarly, terminal and bridging  $\text{PF}_3$  groups have tetracoordinate and pentacoordinate phosphorus atoms, respectively. Thus the phosphorus atom in a bridging  $\text{PF}_3$  group has energetically less favorable hypervalent coordination, necessarily involving high-energy d orbitals or multicenter three-center four-electron bonding. In fact, the  $\text{Co}_2(\text{PF}_3)_8(\mu\text{-PF}_3)$  and  $\text{Cp}_2\text{Fe}_2(\text{PF}_3)_4(\mu\text{-PF}_3)$  having bridging  $\text{PF}_3$  groups without metal-metal bonds may be regarded as substitution products of phosphorus pentafluoride,  $\text{PF}_5$ .



**Figure 7.** Comparison of terminal and bridging CO and  $\text{PF}_3$  ligands showing the hypervalent nature of a bridging  $\text{PF}_3$  group.

## ACKNOWLEDGMENTS

I would like to dedicate this manuscript to Prof. Dr. Luminița Silaghi-Dumitrescu in recognition of her major contributions to Romanian chemistry as well as to many aspects of the research, teaching, and administration at Babeș-Bolyai University during her long career there. In addition her research activities in diverse areas of inorganic, organic, organometallic, and coordination chemistry have had considerable impact beyond the borders of Romania. On a more personal note, my wife (Jane) and I remember with pleasure both her visits to the University of Georgia (USA) as well as adventurous and interesting road trips with her in various parts of southeastern Europe previously unfamiliar to us. The latter include visits to Macedonia (Skopje and Lake Ohrid in 2011), Bulgaria (Sofia and Varna in 2013), and northern Greece (Delphi and Meteora in 2006).



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