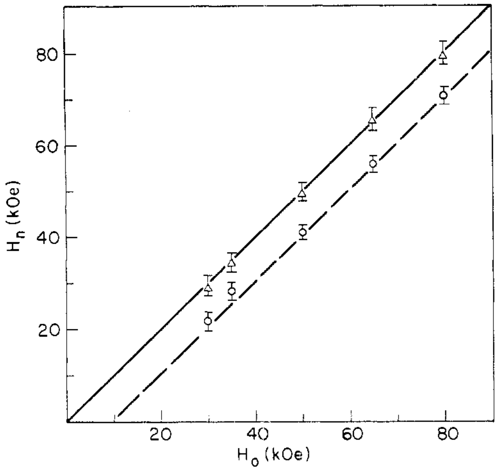

Figure 3. Total field at the nucleus H_n plotted as a function of external field H_0: triangles, $[(\pi\text{-}C_5H_5)Fe(CO)]_4$; circles, $[(\pi\text{-}C_5H_5)Fe(CO)]_4{}^+(PF_6)^-$.

oxidized and reduced forms of the one-iron protein rubredoxin, respectively. Dunham, *et al.*,[8] and Rao, *et al.*,[9] observed hyperfine fields of ~−180 kOe for each of the two sites in the reduced two-iron ferredoxins. In the oxidized form of the four-iron high-potential iron protein from *Chromatium*, Evans, *et al.*,[10] reported hyperfine fields of 121 and 90 kOe. However, direct comparisions between the results obtained in the proteins and the results reported here are not very meaningful because the oxidation states of the iron sites in the present complexes are not known and may not correspond to those in the proteins. Moreover, it is not presently possible to make a quantitiative estimate of the extent of spin delocalization onto the ligands because there are no data or theoretical estimates which give the hyperfine coupling constant per spin in chemical systems of this kind.

The experimental results are consistent with a model for $[(\pi\text{-}C_5H_5)Fe(CO)]_4{}^+$ in which the unpaired electron occupies a delocalized MO at least partly and perhaps largely metal-metal bonding in character. The results agree with a qualitative MO model presented by Toan, Felhammer, and Dahl[11] in conjunction with their crystallographic studies on the $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ and $[(\pi\text{-}C_5H_5)Fe(CO)]_4(PF_6)$ cluster systems. According to this model the highest filled MO's are $e + t_1 + t_2$, formed by appropriate symmetry combinations of iron 3d orbitals. The $e + t_1 + t_2$ orbitals are largely nonbonding with the highest one somewhat antibonding with respect to the metal atoms. In this model, oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ to $[(\pi\text{-}C_5H_5)Fe(CO)]_4{}^+$ occurs by loss of an electron from one of the set of nonbonding orbitals giving the configuration $(e + t_1 + t_2)$.[11] Some spin delocalization onto the carbonyl ligands is expected in this model since the nonbonding $e + t_1 + t_2$ levels are stablized by metal-carbonyl back-bonding.

It is of interest to note that our previous study on the structurally related cluster system $[Fe_4S_4\{S_2C_2(CF_3)_2\}]_4{}^-$ showed essentially no hyperfine interaction. In the singly reduced dithiolate cluster, in which the sulfurs rather than CO groups bridge the iron atoms, the absence of a measurable hyperfine interaction may indicate extensive delocalization onto the ligands. As a consequence the redox properties of the dithiolate cluster may be carried, at least in part, by ligand-based orbitals. Hopefully, work currently in progress on the structurally related clusters $[(\pi\text{-}C_5H_5)FeS]_4$, $[(\pi\text{-}C_5H_5)FeS]_4(PF_6)$, and $[(\pi\text{-}C_5H_5)FeS]_4(PF_6)_2$ will help further to elucidate the electronic structure of these systems.

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Registry No. $[(\pi\text{-}C_5H_5)Fe(CO)]_4$, 12203-87-1; $[(\pi\text{-}C_5H_5)Fe(CO)]_4{}^+(PF_6)^-$, 12791-65-0.

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Contribution from the Department of Chemistry and the
Laboratory for Research on the Structure of Matter,
University of Pennsylvania, Philadelphia, Pennsylvania 19174

Electron Paramagnetic Resonance and Electronic Spectral Evidence for Isomers Resulting from Basal and Axial Ligation of Bis(hexafluoroacetylacetonato)copper(II) by Triphenylphosphine

B. B. Wayland* and V. K. Kapur

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Bis(β-diketonato)copper(II) complexes form a wide variety of five-coordinate 1:1 adducts with neutral donor molecules.[1-14] In many cases the neutral donor occupies the axial position of an idealized square pyramid.[5,6] Epr studies of the mono(pyridine) adduct of bis(hexafluoroacetylacetonato)copper(II) [Cu(Hfacac)$_2$] lead to the proposal that pyridine occupies a basal position in a square pyramid.[7] An X-ray structure determination has proven the occurrence of this type of structure in the 4-aminopyridine adduct of bis(acetylacetonato)copper(II).[8] Pradilla-Sorzano and Fackler have recently reported that Cu(Hfacac)$_2$·H$_2$O diluted into

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Table I. Parameters from Frozen-Solution Epr Spectra for $Cu(Hfacac)_2 \cdot PPh_3$[a]

Solvent	$g_\parallel$	$g_\perp$	$\langle g \rangle$[b]	$A_\parallel(^{63}Cu)$,[c] cm^{-1} (G)	$A_\perp(^{63}Cu)$, cm^{-1} (G)	$a_\parallel(^{31}P)$,[d] cm^{-1} (G)	$a_\perp(^{31}P)$, cm^{-1} (G)
Dichloromethane	2.34	2.06	2.15	0.0146 (134)	0.0014 (14.5)	*e*	
Pentane	2.35	2.07	2.16	0.0149 (136)	0.0014 (15)	*e*	
Methylcyclohexane	2.35	2.07	2.16	0.0147	0.0015	*e*	
Toluene I	2.347	2.0	2.15	0.0152 (139)	0.00143 (15.0)	*e*	
Toluene II	2.255	2.035	2.108	0.0155 (147)	0.00167 (17.5)	0.0121 (115)	0.0162 (170)

[a] Epr parameters from toluene glass spectra for $Cu(Hfacac)_2$ are $g_\parallel = 2.292, g_\perp = 2.05, A_\parallel(^{63}Cr) = 0.01816$ cm^{-1} (171 G), and $A_\perp(^{63}Cu) = 0.00239$ cm^{-1} (25 G). The values for $Cu(Hfacac)_2 \cdot H_2O$ are $g_\parallel = 2.303$, $g_\perp = 2.065$, $A_\parallel(^{63}Cu) = 0.01626$ cm^{-1} (151 G), and $A_\perp(^{63}Cu) = 0.00279$ cm^{-1} (29 G). [b] $\langle g \rangle$ is the average value from frozen-solution data; $\langle g \rangle = {}^1/_3(g_\parallel + 2g_\perp)$. [c] $A(^{65}Cu)$ is also observed and found to equal $1.07A(^{63}Cu)$. [d] $a_\parallel(^{31}P)$ and $a_\perp(^{31}P)$ are the ^{31}P hyperfine coupling constants along and normal to g_z. [e] ^{31}P hyperfine splitting is not observed.

the Zn(II) complex has a $(d_{z^2})^1$ ground configuration[9] which is most consistent with a trigonal-bipyramidal structure. A variety of structures are thus known to occur for five-coordinate 1:1 donor adducts of bis(β-diketonato)copper(II) complexes. However, we are unaware of any well-defined examples of structural isomers in this class of complexes.

Zelonka and Baird have reported on a series of 1:1 trivalent phosphorus donor adducts with $Cu(Hfacac)_2$.[10] Solution epr spectra have been interpreted in terms of relatively large ^{31}P hyperfine splitting. A similar study has recently been reported for the bis(trifluoroacetylacetonato)copper(II)-phosphine adducts.[11] As part of a previous study of 1:1 adducts we examined the epr spectra of $Cu(Hfacac)_2 \cdot PPh_3$ in frozen cyclohexane, dichloromethane, and chloroform and found no ^{31}P hyperfine splitting.[12] This observation suggested that changes in the media might induce $Cu(Hfacac)_2 \cdot PPh_3$ to undergo structural isomerization. In this paper we report on the epr spectra for $Cu(Hfacac)_2 \cdot PPh_3$ in several solution and glass media and interpret the results in terms of isomers in which PPh_3 enters either an axial or a basal coordination position.

Experimental Section

Anhydrous $Cu(Hfacac)_2$ was prepared by the method of Bertrand and Kaplan.[13] The crude product was dried over P_2O_5, vacuum sublimed, and stored over P_2O_5 as desiccant. Pure anhydrous $Cu(Hfacac)_2$ is a dark bluish gray solid. The triphenylphosphine adduct $Cu(Hfacac)_2 \cdot PPh_3$ was prepared by mixing stoichiometric amounts of $Cu(Hfacac)_2$ and PPh_3 in an anhydrous solvent.

Solvents were distilled from P_2O_5 and stored in a vacuum line access bulb over P_2O_5. All preparations were made in an atmosphere of dry, high-purity N_2 gas or on a vacuum line. Samples for epr and electronic spectra were prepared on a vacuum line by distilling solvent into the epr tube containing the sample.

Epr spectra were recorded on a Varian V-4502 X-band spectrometer. Epr spectra were calibrated with DPPH powder. Frozen-solution spectra were recorded from 100 to 130°K.

Electronic spectra were recorded on a Cary Model 14 recording spectrophotometer. Low-temperature electronic spectra were obtained on samples in 4-mm epr tubes frozen to 77°K in a dewar with fused-quartz optical windows.

Results and Discussion

Epr spectra for $Cu(Hfacac)_2 \cdot PPh_3$ in several glass media are reported in Figure 1 and the epr parameters appear in Table I. $Cu(Hfacac)_2$ and the 1:1 adducts should have three different principal *g* values; however, only two ($g_\parallel, g_\perp$) are resolved in frozen-solution media. All frozen-solution spectra for $Cu(Hfacac)_2 \cdot PPh_3$ species have *g* values ($g_\parallel > g_\perp$) indicative of a $(d_{xz}, d_{yz}, d_{x^2-y^2}, d_{z^2})^8 (d_{xy})^1$ ground configuration. Structures of d^9 complexes based on a square pyramid invariably have a $(d_{xy})^1$ configuration[14] and the trigonal bipyramid is generally associated with a $(d_{z^2})^1$ configuration.[15] Epr results cannot, however, be used to distinguish confidently between structures based on a square pyramid or a trigonal bipyramid with weak axial interactions or intermediate geometries.

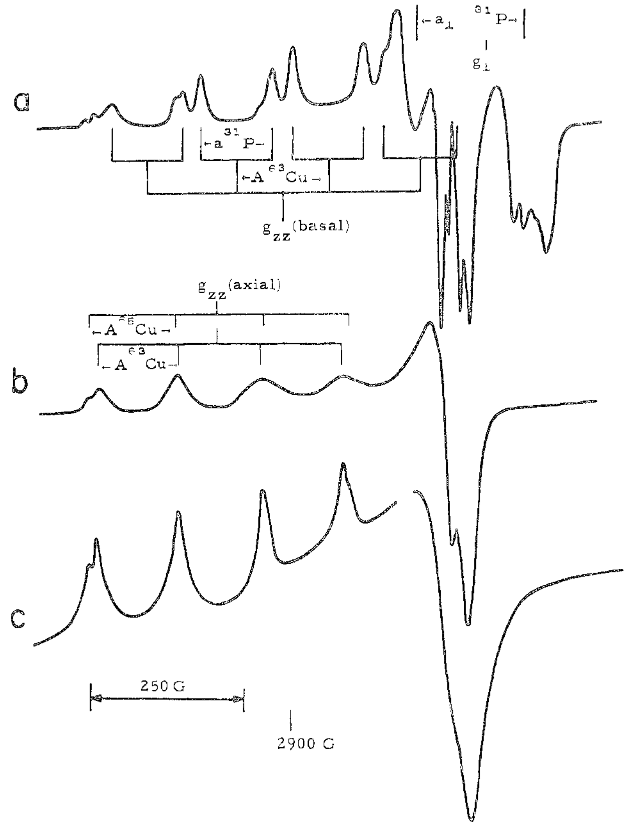

Figure 1. Epr spectra for $Cu(Hfacac)_2 \cdot PPh_3$ in a series frozen solution media (133°K): (a) toluene (the spectra consist of a superposition of transitions for the "basal" and "axial" isomers; the assignment for the g_{zz} region of the "basal" isomer showing the ^{31}P and ^{63}Cu hyperfine coupling is illustrated); (b) methylcyclohexane (the assignment for the g_{zz} region of the "axial" isomer showing ^{63}Cu and ^{65}Cu hyperfine coupling is illustrated); (c) dichlormethane.

For purposes of this discussion, axial and basal ligation will be defined for complexes with a $(d_{xy})^1$ ground configuration as resulting from the neutral donor molecule occupying a position normal to or in the *xy* plane, respectively. The epr criterion for the neutral ligand entering a basal or axial coordination site is the presence or absence of ligand nuclear hyperfine splitting, respectively. The ground configuration for these five-coordinate adducts is $(d_{xy})^1$ so that if the phosphorus donor enters an axial site, very little spin density reaches the donor atom and ^{31}P hyperfine splitting will be very small and probably unresolved. When the donor enters the basal position it binds the copper d_{xy} orbital containing the unpaired electron resulting in substantial phosphorus spin density and associated large ^{31}P hyperfine splitting.

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Frozen-solution epr spectra of $Cu(Hfacac)_2 \cdot PPh_3$ in dichloromethane, pentane, and methylcyclohexane show ^{63}Cu and ^{65}Cu hyperfine coupling but no indication of ^{31}P coupling. An axially ligated structure type is proposed for $Cu(Hfacac)_2 \cdot PPh_3$ in these glass media.

Epr spectra for frozen toluene solutions of $Cu(Hfacac)_2 \cdot PPh_3$ show the presence of two distinct species (Figure 1, Table I). The minor species has epr parameters virtually identical with those of other frozen-solution media and is assigned as the axially ligated complex. The major species present in toluene glass media has distinctly different g and ^{63}Cu hyperfine parameters and large ^{31}P hyperfine splitting (Figure 1, Table I). Epr parameters for this species are consistent with a triphenylphosphine entering a basal coordination position. Toluene glass spectra thus provide epr parameters for two distinct isomeric forms of $Cu(Hfacac)_2 \cdot PPh_3$.

The interrelationships of epr g values and electronic parameters for this ground configuration are given by the approximate expressions[16,17]

$$g_{\parallel} = 2.0023 - 8\lambda\alpha^2\beta^2/\Delta E_{x^2-y^2 \rightarrow xy} \qquad (1)$$

$$g_{\perp} = 2.0023 - 2\lambda\alpha^2\gamma^2/\Delta E_{xy,\, yz \rightarrow xy} \qquad (2)$$

where α^2, β^2, and γ^2 are the fractional d-electron populations in the $b_{2g}(d_{xy})$, $b_{1g}(d_{x^2-y^2})$, and $e_g(d_{xy,\, yz})$ molecular orbitals, respectively. When a planar copper(II) chelate forms a 1:1 adduct with a neutral donor molecule, the $g_{\parallel}$ and $g_{\perp}$ values typically increase and the $A(^{63,65}Cu)$ values decrease.[9,18] The g value increase has been associated with the movement of copper from the chelate donor atom plane and the resulting decrease in $\Delta E_{xz,\, yz \rightarrow xy}$ and $\Delta E_{x^2-y^2 \rightarrow xy}$.[19] The characteristic increase in g values and decrease in ^{63}Cu coupling constants are observed for the proposed axially ligated form of $Cu(Hfacac)_2 \cdot PPh_3$ (Table I). The epr parameters for the proposed basally ligated form of $Cu(Hfacac)_2 \cdot PPh_3$ show the typical reduction in $A(^{63}Cu)$ values, but this species is unusual in having g values less than that of the parent four-coordinate $Cu(Hfacac)_2$ (Table I). The small value for $g_{\perp}$ (2.03) is particularly remarkable and could result from the combined influences of larger σ covalency which reduces α^2 and elevates the d_{xy} mo and π back-bonding which reduces γ^2 and lowers the $d_{xz,\, yz}$ mo (eq 1 and 2).

Electronic spectra for $Cu(Hfacac)_2 \cdot PPh_3$ in dichloromethane and toluene solution (295°K) and glass media (77°K) are reported in Figure 2. Solution electronic spectra in these solvents are similar to those reported by Zelonka and Baird in $CHCl_3$[10] and have a distinctive band centered at 400 nm and a broad-band envelope centered at 675 nm. Isotropic epr spectra in these solvents have large ^{31}P hyperfine splitting (Figure 3) associated with the basally ligated isomer or stereochemically nonrigid species. The 400-nm band present in solution disappears in CH_2Cl_2 glass spectra (Figure 2) where ^{31}P hyperfine splitting is absent in the epr, but this band remains prominent in toluene glass where epr spectra show ^{31}P hyperfine splitting. This distinctive 400-nm electronic transition is thus clearly associated with the species assigned as a basally ligated isomer.

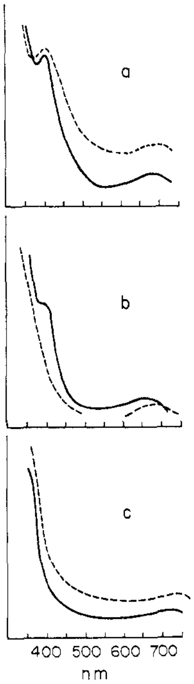

Figure 2. Electronic spectra for $Cu(Hfacac)_2 \cdot PPh_3$ in a series of solution and glass media: (a) toluene; (b) dichloromethane; (c) methylcyclohexane.

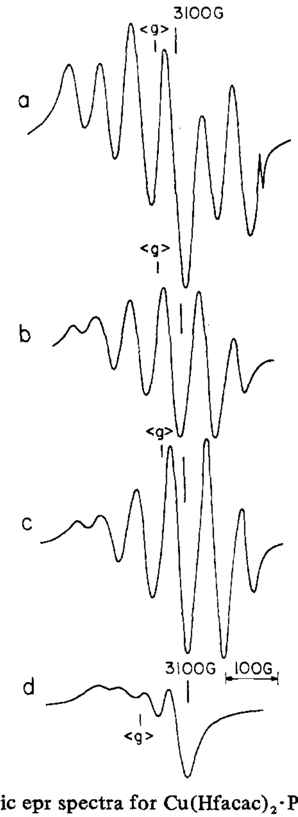

Figure 3. Isotropic epr spectra for $Cu(Hfacac)_2 \cdot PPh_3$ (295°K) in a series of solvents: (a) pentane; (b) dichloromethane; (c) toluene; (d) methylcyclohexane.

Solution epr and electronic spectra for $Cu(Hfacac)_2 \cdot PPh_3$ in methylcyclohexane are unique in not showing ^{31}P hyperfine splitting or the distinctive 400-nm band (Figures 2 and 3). These spectral features associated with the species assigned as the basal isomer are also absent in methylcyclohexane glass (Figure 1). Apparently only the axially ligated $Cu(Hfacac)_2 \cdot PPh_3$ is present in methylcyclohexane solution and glass media.

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Table II. Isotropic Epr Parameters for Cu(Hfacac)$_2$·PPh$_3$ in Organic Solvents[a]

Solvent	$\langle g \rangle$	$\langle A(^{63}Cu) \rangle$, cm^{-1} (G)	$\langle a(^{31}P) \rangle$, cm^{-1} (G)
Dichloromethane	2.137	0.00616 (61.8)	0.01295 (130.0)
n-Pentane	2.136	0.00615 (61.8)	0.01285 (129.0)
Chloroform[b]	2.13	0.00586 (59.0)	0.01311 (132.0)
Toluene	2.138	0.00616 (61.8)	0.01326 (133.0)
Methylcyclohexane	2.165	0.00425 (42.1)	*c*

[a] $\langle g \rangle$, $\langle A \rangle$, and $\langle a \rangle$ are the directly observed isotropic values from solution spectra. The isotropic epr parameters for Cu(Hfacac)$_2$ are $\langle g \rangle = 2.145$ and $\langle A(^{63}Cu) \rangle = 0.0069$ cm^{-1} (69.2 G). [b] Reference 10. [c] ^{31}P hyperfine splitting is not observed.

Epr and electronic spectra for Cu(Hfacac)$_2$·PPh$_3$ in dichlormethane, methylcyclohexane, and toluene solutions and glasses indicate the presence of structural isomers. While toluene solution and low-temperature glass media both contain some basally ligated form, no evidence for the basal isomer is obtained in methylcyclohexane. In dichloromethane the basal form occurs in solution, but only the axial form is observed in the low-temperature glass medium. Observation of a $(d_{z^2})^1$ ground configuration for powders of Cu(Hfacac)$_2$·H$_2$O diluted in the Zn(II) complex[9] and a $(d_{xy})^1$ ground configuration in toluene glass (Table I, footnote *a*) is probably another manifestation of this effect. Medium effects on the observed structural features should be a common occurrence in five-coordinate copper(II) species where the single-hole configuration produces relatively shallow minima in the potential energy surface.

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Registry No. Cu(Hfacac)$_2$·PPh$_3$ (basal), 52049-89-5; Cu(hfacac)$_2$·PPh$_3$ (axial), 37733-67-8.

Contribution from the Department of Chemistry,
Harvard University, Cambridge, Massachusetts 02138

Localized Orbitals in Boron Fluorides. Highly Polarized Boron-Fluorine Double and Triple Bonds

John H. Hall, Jr., Thomas A. Halgren, Daniel A. Kleier, and William N. Lipscomb*

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The boron fluorides form a class of molecules[1] for which very few theoretical studies of the electronic structures are available. Here we present a localized molecular orbital (LMO) description for the valence structures for the boron fluorides BF, BH$_2$F, BF$_2$H, BF$_3$, BF$_2$NH$_2$, B$_4$F$_4$, and B$_2$F$_4$.

The LMO's are obtained by maximizing the sum of squares (SOS) of the distances of orbital centroids from an arbitrarily defined origin[2]

$$D = \sum_{i=1}^{n} [\langle \phi_i | \mathbf{r} | \phi_i \rangle]^2$$

where n is the number of doubly occupied MO's ϕ_i. This procedure, due to Boys, requires only dipole moment integrals. The canonical molecular orbitals (CMO's) are taken from an excellent molecular orbital approximation (PRDDO[3]) to self-consistent field theory. The PRDDO molecular symmetry orbitals are first subjected to a unitary transformation based on random numbers. Then successive 2 × 2 unitary transformations are employed in order to maximize D. This transformation does not change either the total electron density or the energy of the molecule. A second-derivative test, described in detail elsewhere,[4] is performed on each set of LMO's for each molecule in order to ensure convergence to a local maximum on the SOS hypersurface.

Table I. Electronic Populations for Localized Orbitals

Molecule	Interacn[a]	A	A' [b]	A'' [b]	d,[c] %
BF	B-F (1, 3)	0.29	1.71		0
BH$_2$F	B-H (2, 1)	0.91	1.09		9
	B-F (1, 2)	0.44	1.57		3
BHF$_2$	B-H (1, 1)	0.88	1.11		11
	B-F (2, 2)	0.40	1.59		6
BF$_3$	B-F (3, 2)	0.38	1.61		7
BF$_2$NH$_2$	B-F (2, 2)	0.39	1.61		7
	N-H (2, 1)	1.19	0.84		11
	B-N (1, 2)	0.44	1.58		11
B$_4$F$_4$	B-F (4, 3)	0.29	1.71		8
	B-B-B (4, $^2/_3$)	0.66	0.66	0.66	31
BH$_2$F[d]	B-H (2, 1)	0.92	1.09		
	B-F (1, 1)	0.57	1.43		
	B-F (1, 1)	0.21	1.79		

[a] In parentheses (*i, j*) *i* is the number of interactions for the atom pair and *j* is the number of equivalent bonds per contact. For B$_4$F$_4$ there are four equivalent central three-center bonds on the faces of the B$_4$ tetrahedron, yielding $^2/_3$ bond per B-B interaction. [b] Populations are given per equivalent bond for atoms in the order listed in column 2. [c] $d = [0.5\int(\phi^L - \phi^T)^2 \, dv]^{1/2} \times 100\%$, where ϕ^L is an LMO and ϕ^T is ϕ^L modified by setting all nonlocal contributions to ϕ^L equal to zero and renormalizing. [d] Obtained from Edmiston-Ruedenberg localizations.

We describe here highly polar equivalent BF triple bonds in B$_4$F$_4$ and BF double bonds in BH$_2$F, BF$_2$H, BF$_3$, BF$_2$NH$_2$, and B$_2$F$_4$ (Table I). We also include, for comparison, the expected BF triple bond[5] in diatomic BF, which is isoelectronic with CO and N$_2$. However, the triple BF bond in B$_4$F$_4$ is very surprising. The equivalent double and triple bonds obtained for these polyatomic molecules differ in interesting ways from the conventional description of single B-F bonds having some back-donation through the π system.[6] First, all components of a multiple bond in a given BF interaction are equivalent. Second, all components are highly polar, having an excess of electrons on fluorine and leaving atoms neutral within about 0.1-0.2 e of charge (Table I). Hence, even though the Boys LMO and conventional descriptions differ qualitatively, they are both in accordance with the electroneutrality principle.[6] Finally, these multiple bonds are unexpected in the sense that they have not been described previously for BF bonds in polyatomic molecules from conventional valence-bond theory. Regarding the BF axis as a local reference for σ and π bonding, we suggest that these new results are a further illustration, like those of

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