Table II. Isotropic Epr Parameters for $Cu(Hfacac)_2 \cdot PPh_3$ 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 $Cu(Hfacac)_2 \cdot PPh_3$ in dichloromethane, 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 $Cu(Hfacac)_2 \cdot H_2O$ 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.

Acknowledgment. The authors acknowledge support of the National Science Foundation through Grant No. GH-33633.

Registry No. $Cu(Hfacac)_2 \cdot PPh_3$ (basal), 52049-89-5; $Cu(hfacac)_2 \cdot PPh_3$ (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*

Received March 29, 1974 AIC40206N

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_2F, BF_2H, BF_3, BF_2NH_2, B_4F_4, and B_2F_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_2F	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_2NH_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_4F_4	B-F (4, 3)	0.29	1.71		8
	B-B-B (4, $^2/_3$)	0.66	0.66	0.66	31
BH_2F[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_4F_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_4F_4 and BF double bonds in BH_2F, BF_2H, BF_3, BF_2NH_2, and B_2F_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_4F_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

---

(1) P. L. Timms, *Accounts Chem. Res.*, 6, 118 (1973).

(2) (a) S. F. Boys, *Rev. Mod. Phys.*, 32, 296 (1960); (b) J. M. Foster and S. F. Boys, *ibid.*, 32, 300 (1960); (c) S. F. Boys, "Quantum Theory of Atoms, Molecules, and the Solid State," P. O. Lowdin, Ed., Academic Press, New York, N. Y., 1966, p 253.

(3) T. A. Halgren and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.*, 69, 652 (1972); *J. Chem. Phys.*, 58, 1969 (1973). The acronym PRDDO refers to partial retention of diatomic differential overlap.

(4) D. A. Kleier, T. A. Halgren, J. H. Hall, Jr., and W. N. Lipscomb, submitted for publication in *J. Chem. Phys.*

(5) (a) W. England, L. Salmon, and K. Ruedenberg, *Top. Curr. Chem.*, 23, 31 (1971); (b) C. Edmiston and K. Ruedenberg, *J. Chem. Phys.*, 43, S97 (1965).

(6) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 317.

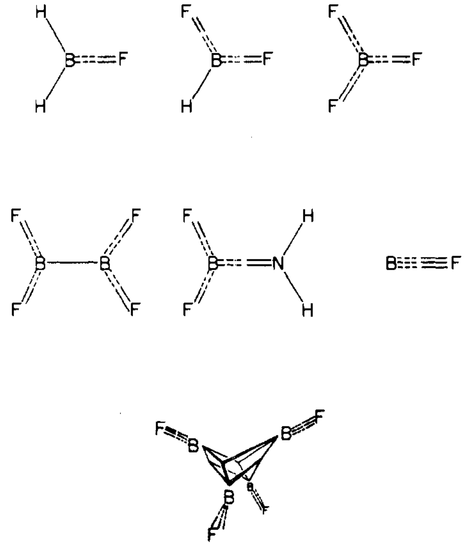

Figure 1. Localized molecular orbitals in BH_2F, BF_2H, BF_3, B_2F_4, BF_2NH_2, BF, and B_4F_4.

benzene,[7] for the preference of LMO's, particularly in Boys' method, for *equivalent* orbitals (τ-like) over a σ-π description. For instance, Edmiston-Ruedenberg (ER)[8] localization of BH_2F results in a bond model displaying σ-π separation and not the equivalent orbital description of the Boys localization (Table I).

The LMO valence structures obtained by Boys' procedure are illustrated in Figure 1. The solid line originates at the atom donating an electron pair and becomes dotted toward the atom which is electron deficient, in order to indicate the bond polarity. The exclusion principle is not violated here inasmuch as only fractions of atomic orbitals are usually employed at an atom for an apparent excess of bonds and lone pairs if present. We call these bonds fractional.[9] This (Boys) LMO description is an equivalent alternative to the usual resonance description, including back-donation of π electrons from lone pairs of F into vacant atomic or molecular orbitals on B.[6] The procedure is objective in its indication of the best single valence structure for electron-pair bonding. The bonding reported here may be typical of a large class of both inorganic and organic[10] molecules which contain lone pairs. For example, the B-N bond in BF_2-NH_2 (Table I) is a highly polarized double bond. Thus electron donation of lone pairs can occur whenever there is a sufficient electron deficiency on a neighboring atom. Moreover, the bonding described here is not restricted to B-F bonds.

Finally, as noted above, the ER localization procedure may show preference for a σ-π description rather than a τ-bond description, as illustrated by the ER localization of BH_2F. An objective preference for the ER method over the Boys method (or *vice versa*) requires some firm experimental or theoretical basis. In 1,2-$C_2B_4H_6$, where the two methods also give different results (a "σ, π" *vs.* a "τ" description[4]), we observe that the ER result yields an *idealized*[11a] three-center bond structure which gives more nearly neutral atoms.[11b] For the molecules presented here a reason for choice is not so clear, and we accept at present both descriptions of the bond models for these molecules. We note that both the ER and Boys localization procedures indicate the participation of lone pairs in bonding. The only ambiguity that remains is whether the actual bonding in the molecule is better described as σ-π or as τ bonding.

Acknowledgments. We are grateful for the Office of Naval Research for support. D. A. K. thanks the National Science Foundation for a postdoctoral fellowship.

Registry No. BF, 13768-60-0; BH_2F, 27944-03-2; BHF_2, 13709-83-6; BF_3, 7637-07-2; BF_2NH_2, 50673-31-9; B_4F_4, 49567-49-9.

[7] M. D. Newton and E. Switkes, *J. Chem. Phys.*, 54, 3179 (1971).

[8] C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, 35, 467 (1963).

[9] D. S. Marynick and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 94, 1748 (1972).

[10] D. A. Kleier, J. H. Hall, Jr., T. A. Halgren, and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.*, in press.

[11] (a) I. R. Epstein and W. N. Lipscomb, *Inorg. Chem.*, 10, 1921 (1971); (b) I. R. Epstein, D. S. Marynick, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 95, 1760 (1973).

Contribution from the Department of Chemistry,
Washington State University, Pullman, Washington 99163

Alkyl- and Arylthioiridium(I) Complexes

Tom Gaines[1] and D. Max Roundhill*

Received April 4, 1974 AIC40223C

Monomeric thioalkyl and -aryl complexes of transition metals are uncommon because of the ready facility for sulfur bridge formation to occur, leading to the isolation of dimers rather than monomers. A number of substituted thioiridium(I) complexes have been recently reported, although in each case the method of preparation appeared to be specific for the compound in question and the authors made no claims as to the generality of the synthetic procedure. The monomeric complex $Ir(C_6F_5)CO(PPh_3)_2$ has been prepared by treating $IrClCO(PPh_3)_2$ with $TlSC_6F_5$[2] or $AgSC_6F_5$.[3] A similar metathetical replacement reaction with $AgSCF_3$ has been used in the synthesis of $Ir(SCF_3)CO(PPh_3)_2$.[4] The nonfluorinated thioiridium(I) complex $Ir(SH)CO(PPh_3)_2$ has been reported and can be prepared by treating $[Ir(CO)(MeCN)(PPh_3)_2]ClO_4$ with either sodium sulfide or H_2S.[5] In view of this recent interest in the synthesis of substituted thioiridium(I) complexes of the type $Ir(SR)CO(PPh_3)_2$, we now describe a general method for the preparation of such compounds for a wide range of functional groups R.

Results and Discussion

We have found that the compounds $Ir(SR)CO(PPh_3)_2$ for the range of R groups Et, *i*-Pr, *n*-Bu, Cy, Ph, and *p*-tol can be conveniently prepared by a single general method. These compounds are bright yellow solids and give monomeric solutions in benzene. They are very soluble in benzene and halocarbon solvents and slightly soluble in ether and lower alcohols. The compounds are prepared by the oxidative ad-

[1] National Science Foundation Summer Undergraduate Research participant from Seattle Pacific University.

[2] M. H. B. Stiddard and R. E. Townsend, *J. Chem. Soc. A*, 2719 (1970).

[3] R. L. Bennet, M. I. Bruce, and R. C. F. Gardner, *J. Chem. Soc., Dalton Trans.*, 2653 (1973).

[4] K. R. Dixon, K. C. Moss, and M. A. R. Smith, *J. Chem. Soc., Dalton Trans.*, 1528 (1973).

[5] C. A. Reed and W. R. Roper, *J. Chem. Soc., Dalton Trans.*, 1370 (1973).