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Calculations and Matrix Infrared Spectra of Terminal Borylene Complexes $FB{=}MF_2$**

*Xuefeng Wang, Björn O. Roos, and Lester Andrews**

Transition metal (M) complexes of boron are characterized by two-center, two-electron bonds between boron and the metal atom. In this classification, transition metal boryl complexes containing M−B single bonds are abundant, but borylene complexes with two M−B bonds are not so thoroughly explored.[1–5] Most borylene complexes are bridged between two metal centers, and there are fewer examples of terminal $L_xM{=}BR$ borylenes. These complexes have large ligands and substituents, and a number of M=B double bonds have been characterized, as described in recent reviews.[5,6] Recent first-row transition metal examples include the terminal $[(OC)_5Cr{=}B{=}N(SiMe_3)_2]$ and $[(\eta^5\text{-}C_5H_5)(OC)_3V{=}B{=}N(SiMe_3)_2]$ complexes and the cationic $[(C_5Me_5)Fe(CO)_2(BMes)]^+$ complex (Mes = 2,4,6-$Me_3C_6H_2$).[6–8] The first and simplest borylene species BF was prepared by Timms from the reaction of BF_3 with solid boron at 2000 °C.[9]

Reactions of laser ablated group 4 transition metal atoms with small molecules have provided many examples of novel bonding situations. First, Ti and CH_3F yielded $CH_3{-}TiF$ and $CH_2{=}TiHF$, which undergo persistent reversible photochemical α-H-transfer rearrangement.[10,11] The methylidene complex exhibits significant agostic distortion.[10–12] Second, Ti and CH_2F_2 produced $CH_2{=}TiF_2$ following C−F insertion and α-F-transfer, and this methylidene complex with a longer double bond is not distorted based on DFT and CCSD calculations.[13] Third, Ti and CF_4 formed the triplet-state electron deficient methylidyne $FC{\equiv}TiF_3$ following C−F insertion and two α-F-transfer rearrangements.[14] Very recently, the triplet nitrene, $N{\equiv}TiF_3$, was produced in the very favorable reaction with NF_3, but the higher energy $FN{=}TiF_2$ imine intermediate in this reaction was not trapped, as these reactions tend to yield the lowest-energy products.[15] The Zr and Hf analogs for the above simple species have also been investigated.[10,11,13–15]

We expect BF_3 to be less reactive than the above precursors owing to very strong B−F bonds, but the possibility of a strong titanium–boron bonding interaction may increase the stability of the $FB{=}TiF_2$ product. Here follows a combined matrix experimental and density functional and wavefunction based theoretical investigation of the first terminal group 4 transition metal borylene complexes.

Boron trifluoride (Aldrich) typically at 0.5 % in argon was reacted with laser ablated Ti, Zr, and Hf metal atoms at much lower concentrations during deposition at 5 K using methods described previously.[10,11,13–15] After reaction, infrared spectra were recorded at a resolution of 0.5 cm^{-1} using a Nicolet 750 spectrometer (Hg-Cd-Te range B detector). Samples were later irradiated for 15 min periods by a mercury arc street lamp (175 W) with the globe removed using a combination of optical filters, and then samples were annealed to allow reagent diffusion.

Infrared spectra for the group 4 metal reaction products with BF_3 are compared in Figure 1. Product absorptions common to all metals include BF_2 at 1398 cm^{-1}, BF at 1374 cm^{-1}, and the HBF_2 absorptions reported previously.[16] The laser ablation plume is also a source of ultraviolet photons for precursor photochemistry. The usual trace of water impurity is the likely origin of hydrogen for the HBF_2 reaction product. New absorptions unique to the titanium reaction appear at 1404, 721, and 638 cm^{-1}, sharpen slightly on annealing to 20 K, and increase slightly on ultraviolet irradiation (Figure 1 a–c). The corresponding spectrum of the zirconium product (Figure 1 d) reveals different bands at

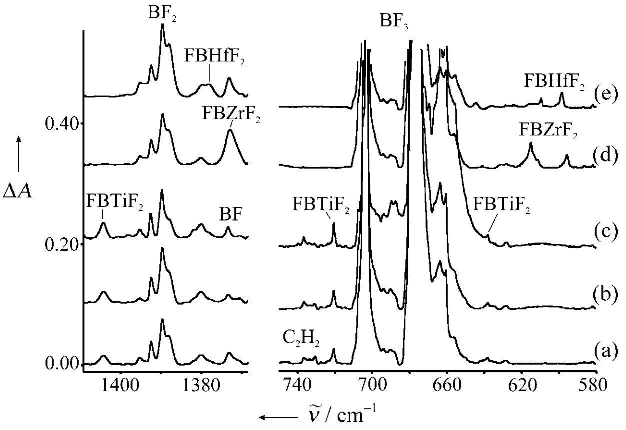

Figure 1. Infrared spectra for group 4 metal atom reaction products with BF_3 in excess argon in the 1410-1370 and 740-580 cm^{-1} regions. a) spectrum after co-deposition of laser-ablated Ti and BF_3 at 0.5 % in argon at 6 K for 60 min, b) after annealing to 20 K, and c) after > 220 nm irradiation for 20 min, d) spectrum after co-deposition of laser-ablated Zr and BF_3 at 0.5 % in argon at 6 K for 60 min, and e) spectrum after co-deposition of laser-ablated Hf and BF_3 at 0.5 % in argon at 6 K for 60 min.

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[*] Dr. X. Wang, Prof. Dr. L. Andrews
Department of Chemistry, University of Virginia
Charlottesville, VA 22904-4319 (USA)
Fax: (+1) 434-924-3710
E-mail: lsa@virginia.edu
Prof. Dr. B. O. Roos
Department of Theoretical Chemistry, Chemical Center, University of Lund, P.O.B. 124, 2-221 00 Lund (Sweden)

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1373, 615, and 596 cm^{-1}, which were not altered by annealing or irradiation. The analogous reaction with hafnium (Figure 1 e) gave absorptions at 1378, 610, and 598 cm^{-1}, and the relative intensities of the latter two are reversed from the zirconium case.

The new higher-frequency bands for each group 4 product species are in the appropriate region for a single B−F stretching mode, but this region is unfortunately too full of other absorptions to observe the ^{10}B signal in natural abundance. Such is not the case for the Th reaction under investigation (not shown here), where the lower B−F stretching frequency at 1276 cm^{-1} allowed the ^{10}B counterpart to be observed at 1318 cm^{-1}. The lower frequency bands fall below the MF_4 molecule (M = Ti, Zr, Hf) absorptions (792, 668, 651 cm^{-1}, respectively), and each pair correlates as expected slightly lower than the antisymmetric and symmetric stretching modes observed for the MF_3 subgroups in the $N{\equiv}MF_3$ nitrene species (782, 705 cm^{-1}; 667, 658 cm^{-1}; 667, 644 cm^{-1}) observed recently.[15] The observation of two M−F stretching modes with such a proximity relationship shows that this new product contains two or three metal–fluoride bonds. The $CH_2{=}MF_2$ molecules have comparable M−F stretching absorptions. Since the B−F region of the spectrum provides evidence for a new BF species, the stoichiometry product that supports these three new bond stretching modes is clearly $FBMF_2$.

Following our work on similar reactions with related small molecules,[10–15] theoretical calculations were performed using the Gaussian 03 program with the B3LYP hybrid density functional and some comparisons with the BPW91 functional.[17–19] The 6-311 + G-(3df) basis was used to represent the electronic density of boron and fluorine, and SDD pseudopotentials were employed for the metal atoms.[20,21] The calculation of vibrational frequencies is not an exact science, and density functional theory (DFT) provides a very good approximation. Calculated frequencies are usually a few percent higher than observed values,[22,23] but that is not always the case.

CASSCF[24] and CASPT2[25] calculations were also performed on the title compounds. The basis set was of VTZP quality with the primitives obtained from the relativistic ANO-RCC basis set (6s5p3d2f1g for Ti, 7s6p4d2f1g for Zr, 4s3p2d1f for F and B).[26,27] Scalar relativistic effects are included in the calculations using the Douglas–Kroll–Hess Hamiltonian as is standard in the MOLCAS software. The active space comprised six orbitals with six electrons chosen to describe the MB σ and π bonds. The bonds to fluorine were assumed to be ionic and were not included. All valence electrons plus the M *n*s and *n*p ($n = 3,4,5$) electrons were correlated in the CASPT2 calculations, which used the standard IPEA Hamiltonian. All calculations were performed with the MOLCAS-7 quantum chemistry software.[28] The geometries for both singlet and triplet states were optimized at the CASPT2 level, and vibrational frequencies were computed using numerical gradients and Hessians. All calculations were performed in C_s symmetry, but the resulting geometries had C_{2v} symmetry, except for the Hf singlet product, which is slightly distorted out of plane.

Tables 1 and 2 compare the observed and computed frequencies using CASPT2 and DFT methods for the three singlet $FB{=}MF_2$ borylene transition metal difluoride products. The B3LYP frequencies are all slightly higher than the observed values, and the BPW91 values are slightly lower, as expected.[22,23] The frequencies calculated by CASPT2 are

Table 1: CASPT2 calculated vibrational frequencies (in cm^{-1}) and vibrational intensities (in km mol^{-1}) within parenthesis.

		Ti($^1A_1$)	Ti($^3A_2$)	Zr($^1A_1$)	Zr($^3A_2$)	Hf($^1A'$)	Hf($^3A_2$)
B−F str	a_1	1454(403)	1457(670)	1422(468)	1409(426)	1420(581)	1429(343)
expt.		1404		1373		1378	
M−F str	b_2	755(284)	666(311)	638(256)	604(244)	654(76)	616(85)
expt.		721		615		598	
M−F str	a_1	670(151)	624(183)	618(102)	593(125)	643(201)	604(172)
expt.		638		596		610	
M−B str	a_1	421(8.0)	428(1.9)	405(9.2)	421(8.7)	383(5.2)	421(16)
MBF def	b_1	318(19)	278(1.2)	267(5.7)	275(5.9)	339(13)	283(9.8)
MBF def	b_2	314(3.7)	276(0.6)	267(5.7)	265(1.3)	306(0.1)	229(7.5)
MF_2 bend	a_1	148(19)	135(19)	121(17)	132(16)	136(16)	131(15)
FBMF def	b_2	103(54)	109(24)	85(1.8)	88(3.3)	91(1.9)	77(0.6)
BMF_2 def	b_1	88(0.8)	71(2.0)	73(1.4)	73(2.3)	65(22)	71(1.5)

Table 2: Observed and DFT calculated fundamental frequencies of the group 4 transition metal $FB{=}MF_2$ borylene molecules in the ground $^1A_1$ electronic states with C_{2v} structures.[a]

Mode (approx.)	$FB{=}TiF_2$					$FB{=}ZrF_2$			$FB{=}HfF_2$		
	obs	calcd	int	calcd(BP)	int(BP)	obs	calcd	int	obs	calcd	int
B−F str, a_1	1404	1444	424	1394	341	1373	1413[b]	432	1378	1409[c]	607
M−F str, b_2	721	742	243	736	219	615	641[b]	209	598	615[c]	156
M−F str, a_1	638	656	108	654	101	596	608[b]	91	610	612[c]	53
M−B str, a_1		398	0	405	0		381[b]	1		374[c]	1
MBF def, b_1		325	23	318	29		334	32		344	13
MBF def, b_2		321	4	311	2		311	0		315	0
MF_2 bend, a_1		133	11	141	8		130	9		124	12
FBMF def, b_2		79	0	83	0		86	1		88	1
BMF_2 def, b_1		48	25	24	32		45	32		55	71

[a] Frequencies and intensities are in cm^{-1} and km mol^{-1}, respectively. Observed in an argon matrix. Frequencies and intensities calculated with B3LYP/6-311 + G(3df) in the harmonic approximation using the SDD core potential and basis set for metal atoms. Mode symmetry notations are based on the C_{2v} structure. Calculations using the BPW91 functional gave similar frequencies noted (BP) for the titanium product. [b] Calculations using the BPW91 functional gave 1371(345), 635(192), 603(81), 381 cm^{-1}(3 km mol^{-1}). [c] Calculations using the BPW91 functional gave 1379(324), 603(151), 601(72), 376 cm^{-1}(5 km mol^{-1}).

slightly higher than the B3LYP values: a similar relationship among computed frequencies for these different methods has been found for the simple group 6 metal pnictides.[29] In the case of $FBTiF_2$, the B3LYP computed terminal bond stretching frequencies are 2.8, 2.9, and 2.8 % higher, for $FBZrF_2$ the calculated values are 2.0–4.2 % higher, and for $FBHfF_2$ the computed frequencies are 0.3–2.0 % higher and again the BPW91 values are slightly lower. Overall the agreement between calculated and observed frequencies is excellent, and this correlation confirms our identification of the first Ti, Zr, and Hf borylene complexes.

Previous work on similar reactions with related small molecules[10–15] suggests that the reaction proceeds through insertion and then α-F-transfer according to reaction (1).

$$M(^3F) + BF_3 \rightarrow F_2B{-}MF \rightarrow FB{=}MF_2 \qquad (1)$$

Reaction (1) is exothermic by 56, 41, and 38 kcal mol^{-1} at the CASPT2 level of theory for the singlet Ti, Zr, and Hf reaction products $FB{=}MF_2$, respectively, with basis set superposition error (BSSE) of 3 kcal mol^{-1} included. The larger binding energy for the Ti borylene is likely due to the smaller size of the Ti orbitals, which fit better with the B orbitals. A second α-F-transfer does not proceed as the $BTiF_3$ product has even higher energy than the reagents.

The structures of the three group 4 borylene complexes are illustrated in Figure 2, and the bond lengths and angles are listed in Table 3. The B3LYP and BPW91 hybrid and pure density functionals and CASSCF/CASPT2 wavefunction methods give very similar structural parameters, which is reassuring. The CASSCF/CASPT2 computed Ti=B bond length (2.094 Å) is about 5 % longer than from X-ray measurements (1.996 and 1.959 Å, respectively) for the $[(OC)_5Cr{=}B{=}N(SiMe_3)_2]$ and $[(\eta^5\text{-}C_5H_5)(OC)_3V{=}B{=}N(SiMe_3)_2]$ complexes,[6,7] which is reasonable for this early transition metal. Similar DFT calculations (BP86 functional) find good agreement with measured bond lengths for iron borylene complexes.[30] The Hf–F and Hf=B bonds are slightly shorter than the Zr–F and Zr=B analogs as befits the well-known effects of relativity on this closely related pair of transition metal atoms.[31] The computed B–F bonds are slightly longer than the BF diatomic molecule value (1.262 Å)[32] increasing from 1.274 to 1.284 to 1.286 Å (B3LYP values) in the $FB{=}TiF_2$, $FB{=}ZrF_2$, and $FB{=}HfF_2$ series of molecules, respectively. We suggest that hyperconjugation of the fluorine lone pair in bonding with boron is facilitated by the (p–d) π interaction between boron and the metal center, which is more favorable for the smaller Ti(3d) orbitals. The Ti and Zr species have real frequencies in the C_{2v} equilibrium symmetry. The singlet state in the Hf compound is a little bit different from the others: the symmetry is no longer C_{2v} but only C_s with the HfF_2 group tilted slightly out of plane, which is unique to this metal.

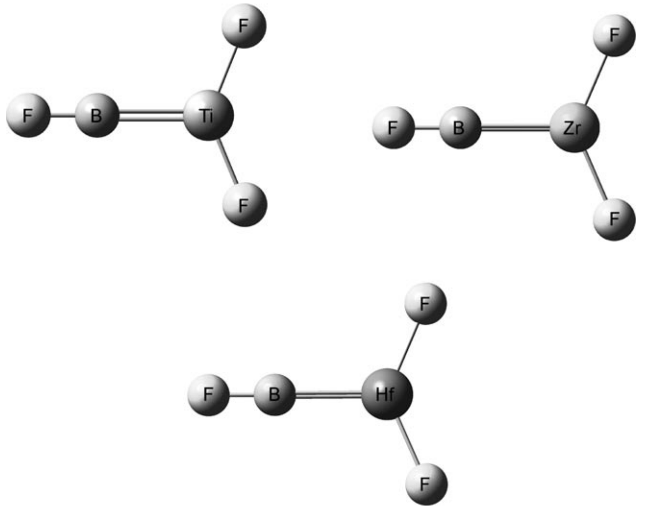

Figure 2. Structures calculated for the group 4 transition metal difluoride borylene complexes using B3LYP, BPW91, and CASSCF/CASPT2 methods. The structures are C_{2v} for $FB{=}TiF_2$ and $FB{=}ZrF_2$ and C_s for $F{=}HfF_2$.

Table 3: Structural parameters for the singlet ground state $FB{=}MF_2$ (M = Ti, Zr, Hf) borylene molecules.[a]

Parameter	$FB{=}TiF_2$	$FB{=}ZrF_2$	$FB{=}HfF_2$
r(B=M)	2.097/2.085/2.094	2.223/2.216/2.220	2.210/2.197/2.156
r(M-F)	1.800/1.795/1.789	1.952/1.951/1.923	1.942/1.946/1.898
R(B-F)	1.274/1.290/1.287	1.284/1.297/1.293	1.286/1.300/1.297
∡(FMF)	138.3/135.6/139.7	135.3/133.5/137.0	130.8/133.7/135.8
∡(FMB)	110.8/112.2/110.2	111.9/113.2/111.5	111.5/113.2
BE[b]	56	41	38

[a] Bond lengths and angles are in Å and degrees are given for the singlet states from B3LYP/BPW91/CASPT2 calculations. The $FB{=}TiF_2$ molecule converges in C_{2v} symmetry in all three calculations, $FB{=}ZrF_2$ converges likewise save it is slightly distorted with B3LYP, and $FB{=}HfF_2$ is slightly distorted in B3LYP and CASSCF/CASPT2 calculations. [b] Binding energy from CASPT2 in kcal mol^{-1} relative to M + BF_3 including BSSE correction (3 kcal mol^{-1}).

The geometry was optimized for the singlet and triplet states of $FB{=}TiF_2$, $FB{=}ZrF_2$, and $FB{=}HfF_2$ at the CASSCF/CASPT2 level of theory (structural parameters are given for both states in the Supporting Information). The triplet state was found to be located 8.2 kcal mol^{-1} for M = Ti, 10.4 kcal mol^{-1} for M = Zr, and 8.2 kcal mol^{-1} for M = Hf above the singlet ground state.

The natural orbitals with their occupation numbers are shown in Figure 3 both for the singlet and the triplet states of the titanium compound (the orbitals for the Zr and Hf borylenes are very similar and will not be shown). The top row gives the orbitals for the singlet state. We note the formation of a double bond with an effective bond order (EBO) of 1.81 for Ti, 1.86 for Zr, and 1.90 for Hf. For the triplet state, the two-electron π bond is replaced by two π type one-electron bonds, one out of plane and one in the plane. This is very similar to the bonding in the $^3\Sigma_g^-$ ground state of the B_2 molecule with the electronic configuration $(\pi_u)^2$. The EBO for this state is actually somewhat larger, 1.87 for Ti and 1.92 for Zr, and 1.94 for Hf even if it is a little bit higher in energy. Table 4 summarizes the orbital occupancies for both singlet and triplet states for the group 4 borylene molecules. It seems that two one-electron bonds are slightly more effective in

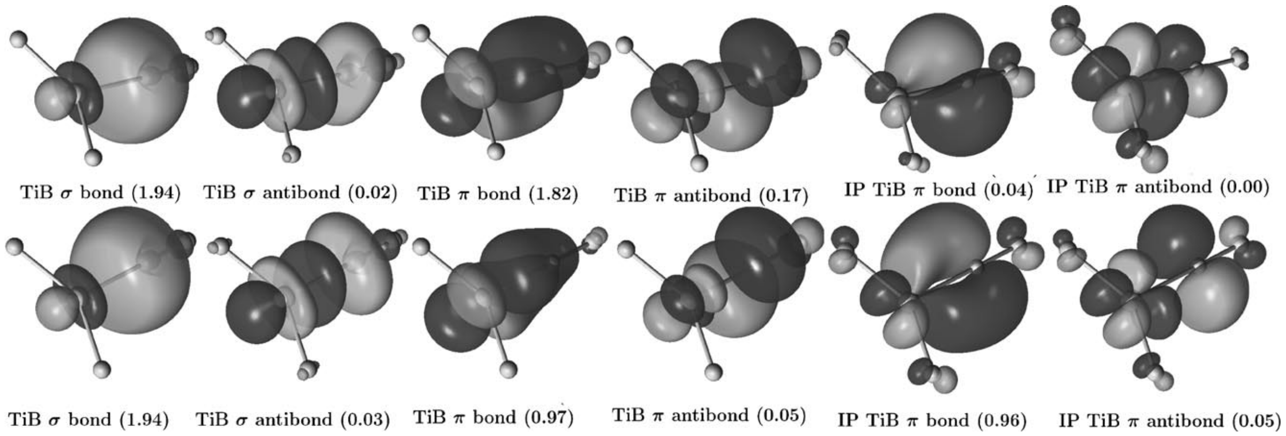

Figure 3. The active molecular orbitals in FB=TiF$_2$ for the singlet (top row) and the triplet states. The contour line used is 0.05 e au^{-3}. MO occupation numbers are given with each orbital.

Table 4: Natural orbital occupation numbers computed by CASSCF/CASPT2 for the active orbitals of the FB=MF$_2$ borylene molecules in singlet and triplet electronic states.

Orbitals	Ti($^1A_1$)	Ti($^3A_2$)	Zr($^1A_1$)	Zr($^3A_2$)	Hf($^1A'$)	Hf($^3A_2$)
a_1 (σ)	1.94	1.94	1.94	1.95	1.94	1.96
a_1 (σ*)	0.02	0.03	0.02	0.03	0.02	0.02
b_1 (π)	1.82	0.97	1.90	0.99	1.92	0.99
b_1 (π*)	0.17	0.05	0.10	0.03	0.08	0.02
b_2 (π in pl)	0.04	0.96	0.04	0.99	0.04	0.99
b_2 (π* in pl)	0.00	0.05	0.00	0.02	0.00	0.02
EBO	1.81	1.87	1.86	1.92	1.90	1.94

bonding than the two-electron π bond although the triplet state is higher in energy.

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