Borylene Complexes

DOI: 10.1002/anie.201000841

Fashionably Late: Synthesis and Characterization of Transition-Metal–Fluoroborylene Complexes**

Holger Braunschweig and Rian D. Dewhurst*

boron · borylene complexes · Group 4 metals · matrix isolation · ruthenium

The neutral diatomics of the first-row main-group elements, that is, N_2, CO, and BF, span a remarkably large reactivity continuum despite their isoelectronic relationship, and this discrepancy translates faithfully to the field of transition metal chemistry. The major challenge in binding dinitrogen to transition metals is its extreme inertness, whilst CO, metastable but storable under ambient conditions, is now frequently described as "ubiquitous" as a ligand in transition metal complexes.[1a] Like N_2, the third diatomic of the series, BF, has been difficult to bind to transition metals, but for the opposite reason: its extreme reactivity has rendered it difficult to generate and/or stabilize in the coordination sphere of a metal. Consequently, BF has attracted much synthetic and theoretical interest owing to the absence of its transition metal chemistry.

The search for an explanation of these observations according to energetic behavior was first expounded upon in 1998 in two publications from Baerends and Hoffmann,[1] the first of which evaluated the energy of the frontier orbitals of the free ligands. The energy of the LUMO orbital of each was found to remain relatively unchanged, whereas the HOMO orbital climbed dramatically in energy with increasing bond polarity ($N_2 < CO < BF$; Figure 1). Consequently, BF readily forms thermodynamically strong σ bonds to transition metals, but the extent of the $B \rightarrow M$ electron donation leaves the boron atom with residual positive charge and thus it is kinetically vulnerable. This theory has thus far been vindicated: successful syntheses of terminal borylene complexes ($M{=}BX$) have required the use of substituents with π-donor ability or steric bulk.[2] In the proposed fluoroborylene ligand, the fluoride substituent is a comparable π donor to oft-used di(alkyl/silyl)amino groups, but is hardly intimidating from a steric viewpoint. In three recent reports, these problems have however been cleverly circumvented. By applying higher metalation[3] and matrix isolation,[4] the groups of Aldridge and Andrews have presented the definitive syntheses of a number of fluoroborylene complexes.

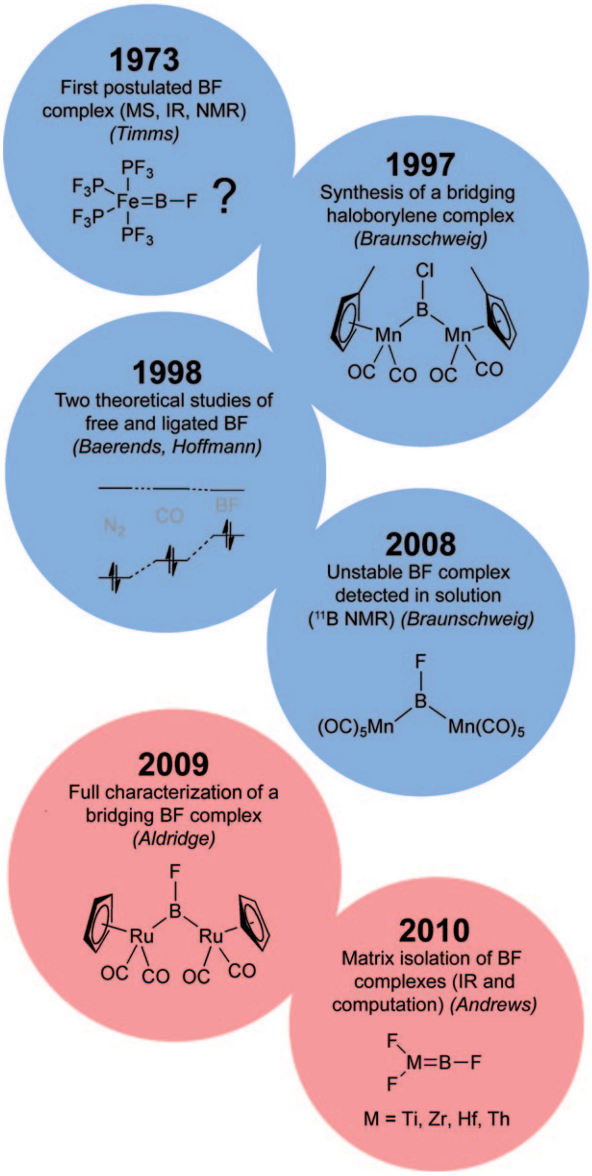

Figure 1. Timeline showing the development of BF as a ligand.

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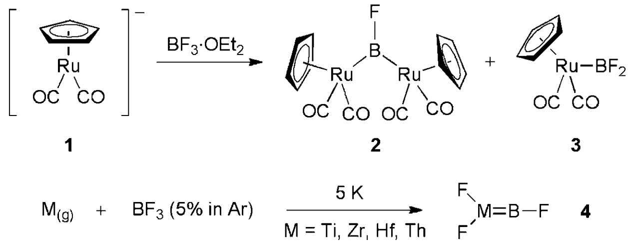
[*] Prof. Dr. H. Braunschweig, Dr. R. D. Dewhurst
Institut für Anorganische Chemie, Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
Fax: (+49) 931-888-4623
E-mail: h.braunschweig@mail.uni-wuerzburg.de
Homepage: http://www-anorganik.chemie.uni-wuerzburg.de/Braunschweig/index.html

[**] H.B. thanks the Deutsche Forschungsgemeinschaft (DFG) for continued financial support. R.D.D. is grateful to the DFG for an independent research grant.

The first report of a postulated fluoroborylene complex was from Timms in 1973, as a culmination of his work on the generation of free BF.[5] One product of co-condensation of B_2F_4, PF_3, and iron vapor was unstable above −50 °C, and was assigned the formula $[Fe(BF)(PF_3)_4]$ based on mass spectrometry, and IR and ^{19}F NMR spectroscopy. Later, after the synthesis of the first bridging aminoborylene complex,[6a] a bridging chloroborylene complex, $[\{(\eta^5\text{-}C_5H_4Me)(OC)_2Mn\}_2BCl]$ was synthesized and fully characterized,[6b] and a putative bridging fluoroborylene complex $[\{(OC)_5Mn\}_2BF]$ was detected (based on ^{11}B NMR) in 2008.[7]

Aldridge and co-workers report that addition of $BF_3{\cdot}OEt_2$ to $Na[(\eta^5\text{-}C_5H_5)Ru(CO)_2]$ (**1**) resulted in a mixture of fluoroborylene $[\{(\eta^5\text{-}C_5H_5)(OC)_2Ru\}_2(\mu\text{-}BF)]$ (**2**) and boryl $[(\eta^5\text{-}C_5H_5)(OC)_2Ru(BF_2)]$ (**3**) complexes by double and single salt metathesis, respectively (Scheme 1).[3] In diethyl ether, the fluoroborylene complex **2** is favored over boryl complex **3** nine-fold; however, when the solvent was replaced with toluene, this preference was inverted. After isolation of **2**, corresponding coupling patterns in the ^{11}B and ^{19}F NMR spectra (doublet and quartet, respectively; $J_{BF} = 247$ Hz) suggested a direct B−F bond, and the X-ray crystallographic study confirmed this proposal.



Scheme 1. Synthetic routes to fluoroborylene complexes.

Subsequent fluoride abstraction by $AlCl_3$ led to the cationic diruthenaboride complex $[\{(\eta^5\text{-}C_5H_5)(OC)_2Ru\}_2(\mu\text{-}B)]^+$, an analogue of a previously reported iron complex.[7] To provide a direct comparison of BF and CO ligand reactivity, $AlCl_3$ was added to the related complex $[\{(\eta^5\text{-}C_5H_5)(OC)Ru\}_2(\mu\text{-}CO)_2]$; this reaction resulted not in abstraction of a carbonyl oxygen atom but rather a Lewis acid–base pair with an Al−O bond.

Independently, in two separate reports, Andrews and co-workers disclosed the reaction of metal vapor with BF_3 to give fluoroborylene complexes of Ti, Zr, Hf, and Th—four metals for which no stable borylene complexes was known (Scheme 1).[4] In fact, the first complexes containing Ti−B and Hf−B bonds were only synthesized very recently,[8] and such examples are still unknown for Zr and Th. By allowing the two reagents to mix at 5 K during deposition, irradiating, and annealing, the resulting complexes $[F_2M{=}BF]$ (**4**; M = Ti, Zr, Hf, Th) were detected by infrared spectroscopy in an argon matrix. Comparison of the IR spectra with computationally predicted vibrational frequencies confirmed the presence of the target complexes.

With the synthesis of fluoroborylene complexes comes expectation for insight into their properties. Aldridge and co-workers showed that the B−F distance in **2** (1.348 Å) is well within the range expected for difluoroboryl complexes $[L_nM{-}BF_2]$, which is unsurprising in that both feature planar, three-coordinate boron atoms. Calculations by the group of Andrews found that in all cases, the reaction leading to their fluoroborylene complexes is exothermic ($M + BF_3 \rightarrow$ **4**; M = Ti: 56, M = Zr: 41, M = Hf: 38, M = Th: 40 kcal mol^{-1}), the larger binding energy for titanium being ascribed to better overlap of the orbitals of Ti and B. The observed and calculated B–F stretching frequencies in **4** were found to decrease as the row is descended (observed: M = Ti: 1404, M = Th: 1276 cm^{-1}). The values are found to either side of the calculated vibrational frequency of free BF (1358 cm^{-1}).[1b] Similarly, the effective bond order calculated for M−B increased (M = Ti: 1.81, M = Th: 1.91), indicating more effective π backbonding and a weakening of the B−F linkage.

The recent contributions by Aldridge and Andrews, taken together, are a complementary synthetic coup. Using two starkly contrasting strategies, the BF ligand has been achieved in both late-transition-metal/electron-rich and early-transition-metal/electron-poor coordination environments. Together, the reports have definitively closed the file in the case of the missing fluoroborylene complex, allowing the focus to shift to determining the properties and reactivity of this unusual ligand, the last of the neutral first-row main-group diatomics.

Received: February 10, 2010

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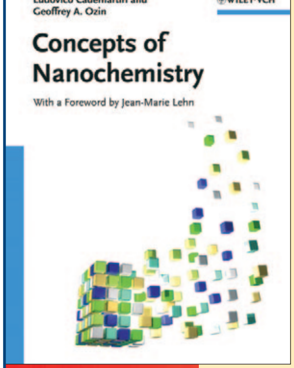
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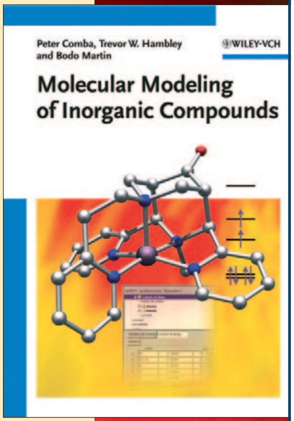
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