

Quadruple Bonding involving Main Group Elements.

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Before the landmark discovery of quadruple bonds in rhenium complex, $K_2[Re_2X_8] \cdot 2H_2O$, by Cotton and coworkers in 1964, threefold bond was assumed to be the highest bond multiplicity.¹ It was also the first time a new type of bond (δ) was observed. These quadruple bonds occur due to available non-bonding d-electron(s) and justifies why it is only possible in transition metals.² The number of possible metal-metal bond depends on the number of d-electrons available for bonding. Various transition metal dimers with multiple bonds, ranging from four to sixfold have been reported.^{1,3-5} Unsaturation about a metal center is a desired feature in the generation of a catalytic cycle, and to promote reactions which are impossible.⁶

On the other hand, main group elements can involve in a maximum bond order of three due to the number of available valence orbitals (ns, np) for bonding, although this is rare in heavier congeners in the same group.⁷ Threefold bonding in boron, stabilized by donation from the ligand orbital to the empty orbitals on boron had been reported. The resulting homonuclear boron-boron complex, $(NHC) \rightarrow B \equiv B \leftarrow (NHC)$, found to be efficient for small molecule activation was a breakthrough in main group chemistry.^{7,8}

Extending this scope, one might ask if main group elements with no d-electrons can be quadruple bonded. Or if the valence orbitals in main group elements can overlap with the d-orbitals in transition metals to give a bond order of four. Molecules that can exemplify these properties could challenge the traditional view on molecular bonding, invoke similar reactivities as the transition metals and could present a whole new variety of systems to explore in the area of main group catalysis.⁹ Quadruple bonding in representative elements is a subject of intense debate since the work on C_2 and its isoelectronic diatomic eight-valence electron species in 2012.

C_2 does not involve a metal. However, it served as the basis for the recent advances and interests in fourfold bonds in main-group elements. Due to the lack of diradicaloid character in C_2 , Shaik *et.al.* computed the properties of the inverted fourth bond using the valence bond (VB) theory and full configuration interaction (FCI).¹⁰ The bond energy of the putative fourth bond was found to be 12 – 15 kcal mol⁻¹ by different methods which agree with the experimental value of 13 kcal mol⁻¹. The results also showed a total bond energy of 303 kcal mol⁻¹, compared to a value of 270 kcal mol⁻¹ observed for the triply bonded HCCH. The computed bond order in HCCH and C_2 was 3.714 and 2.998 respectively. Most of the computed and experimental properties are in good agreement, and presented a strong argument for the inverted fourth bond. However, computed the force constant was a setback in this study. Triply bonded HCCH gave a force constant of 16 N

m^{-1} whereas that of C_2 was 12 N m^{-1} .¹⁰ Though a methodological explanation was presented, there was no chemical explanation for this observation.

Jun et. al in 2019 reported a quadruple bonding between boron and iron in $\text{BFe}(\text{CO})_3^-$. This complex was synthesized in gas phase and characterized by mass-selected infrared photodissociation spectroscopy. Quantum chemical and experimental investigations confirmed a C_{3v} symmetry with the CO ligands attached to the iron center. The observed equilibrium B–Fe distance of 1.63 \AA suggests a B–Fe order higher than three when compared to other complexes with a similar bond. The bonding interaction involves an electron-sharing σ bond, two $\text{Fe} \rightarrow \text{B}$ π bonds and a $\text{B} \rightarrow \text{Fe}$ σ bond (Figure 1a), giving a fourfold bond that involves a main group atom.⁹ However, the role of the $\text{Fe}(\text{CO})_3^-$ fragment and its effect in this bonding network was underemphasized.

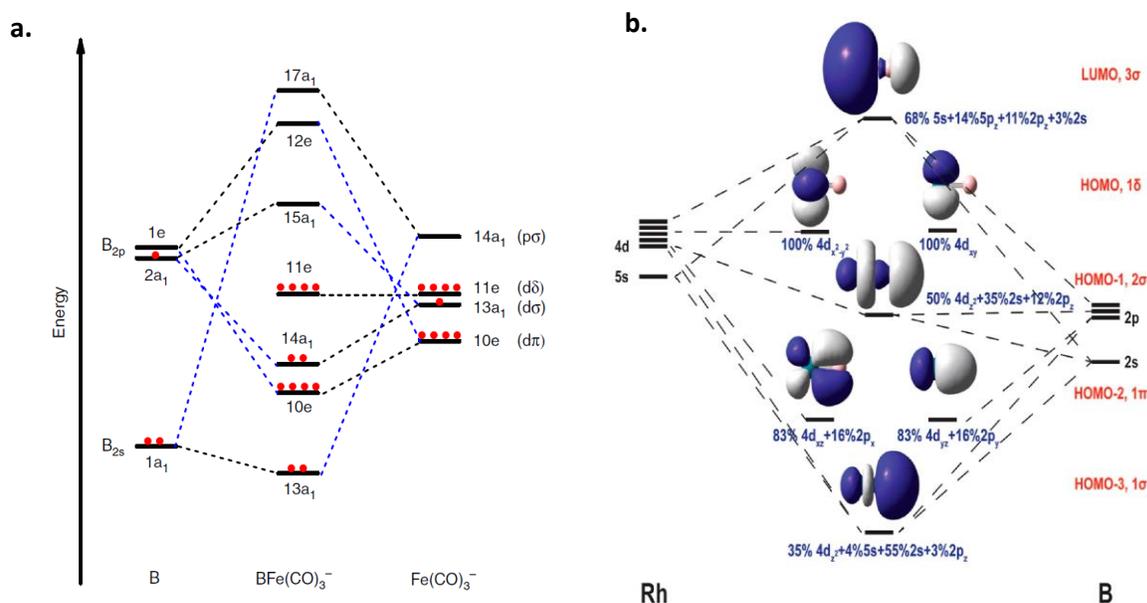


Figure 1 a) Bonding scheme of the C_{3v} structure of $\text{BFe}(\text{CO})_3^-$. The scheme qualitatively illustrates the bonding interactions between boron $2s$ - $2p$ orbitals and Fe $3d/4p$ orbitals in the $\text{Fe}(\text{CO})_3^-$ fragment (Adapted from Ref. 9) b) MO diagram and MO atomic compositions for RhB (Adapted from Ref. 11).

Recently in 2021, Wang and coworkers used photoelectron spectroscopy and computational methods to probe the electronic structure and bonding in RhB^- and RhB . Bond order analysis revealed two σ and two π quadruple bonds that are significantly based on B and Rh atomic orbitals (Figure 1b). A slight decrease in bond multiplicity was observed as we move from RhB to RhB^- which is consistent with an additional electron residing in antibonding molecular orbital.¹¹

These works are foundational and serve as prospects for future work. These could open door to a variety of compounds that are yet to be explored. The reactivity of the quadruple bonded main group atoms could also present a new scope in the area of main group catalysis.

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