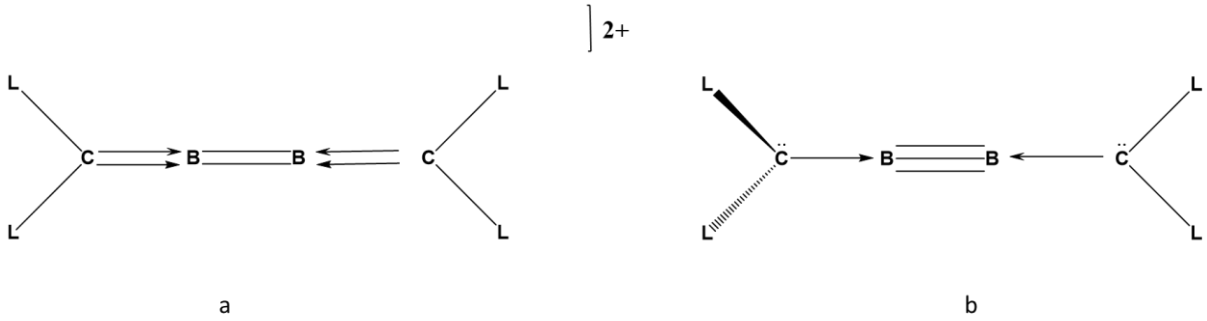
Carbone Supported Diboron Compounds - Structure and Bonding of $[B_2[C(L_2)]_2]^{2+}$ and $[B_2[C(L_2)]_2]$ (L = CO, NHC, PMe_3 and cAAC)

Jishnu Sai G, Naseeha V T and Pattiyil Parameswaran*

National Institute of Technology Calicut, Department of Chemistry, India-673601

Email: jishnusai.upasana@gmail.com, Ph: +919746604646

The stabilisation of diboron has been an intriguing research area in chemistry. [1] The molecular orbital theory suggests that B_2 has two half B-B π bonds and B_2^{2+} has no B-B bonds similar to that of Be_2 molecule. This bonding situation can be altered by coordinating with electron-donating ligands on the diboron moiety. There are many attempts to stabilise diboron compounds in various oxidation states with many supporting ligands such as CO, NHC etc. Here we have studied the effect of coordinated carbones on B-B bonding in diboron. Accordingly, the structure and bonding of carbone supported dicationic ($[B_2[C(L_2)]_2]^{2+}$) and neutral ($[B_2[C(L_2)]_2]$) diboron compounds (L = CO, NHC, PMe_3 and cAAC) were carried out at the M06/def2-TZVPP//BP86/def2-TZVPP level of theory. $[B_2[C(L_2)]_2]^{2+}$ has singlet cumulenic equilibrium geometry when L = CO, NHC and PMe_3. The molecular orbital (MO) analysis indicates that the C-B-B-C skeleton is similar to that of butatriene viz. one localised B-B π MO and two delocalised C-B-B-C π MOs when L = CO, NHC and PMe_3. Hence the carbones act as a four-electron donor ligand (Scheme 1a). On the other hand, $[B_2[C(L_2)]_2]^{2+}$ has triplet allenic geometry when L = cAAC. Since cAAC is a good π acceptor ligand, CL_2 (L = cAAC) act as only two electron donor ligand. As a result, B-B bond enforces to form two half π bonds along with a σ bond. The geometrical analysis indicates that neutral $[B_2[C(L_2)]_2]$ have singlet allenic type equilibrium geometry with a B-B bond length in the range of triple bond length for all ligands. The MO analysis indicates that there are two localised π bonds apart from the B-B σ bond. Hence carbones act as a two-electron σ donor ligand. (Scheme 1b)



Scheme 1. Qualitative bonding representation of (a) $[B_2[C(L_2)]_2]^{2+}$, L = CO, NHC and PMe_3 and (b) $[B_2[C(L_2)]_2]$ L = CO, NHC, PMe_3 and cAAC

References

1. E. C. Neeve , S. J. Geier , I. A. I. Mkhalid , S. A. Westcott and T. B. Marder , *Chem. Rev.*, 116 (**2016)** 9091-9161.