Electronic Supplementary Material (ESI) for RSC Advances.

Noble Gas Supported B_3^+ Cluster: Formation of Strong Covalent Noble Gas-Boron Bonds

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SUPPORTING INFORMATIONS

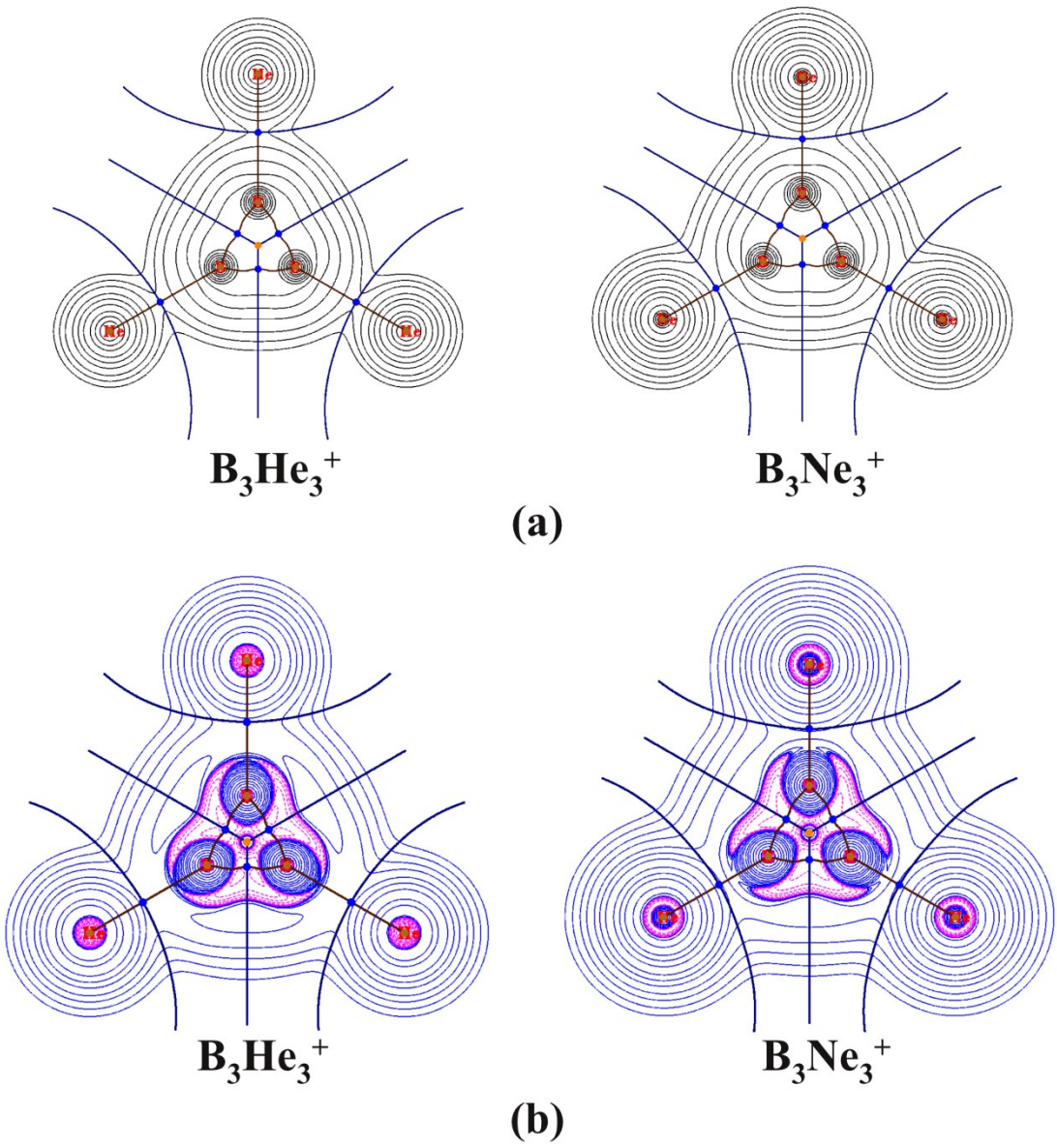

Fig. 1-SI Contour plots of (a) electron density and (b) Laplacian of the electron density ($\nabla^2\rho(\mathbf{r})$) of $B_3Ng_3^+$ (Ng = He, Ne) clusters at the MP2/def2-TZVP/WTBS level. (Black solid lines in (a) shows $\rho(\mathbf{r})$ contours; blue solid lines and magenta dashed lines in (b) show the region with $\nabla^2\rho(\mathbf{r}) > 0$ and region with $\nabla^2\rho(\mathbf{r}) < 0$ respectively)

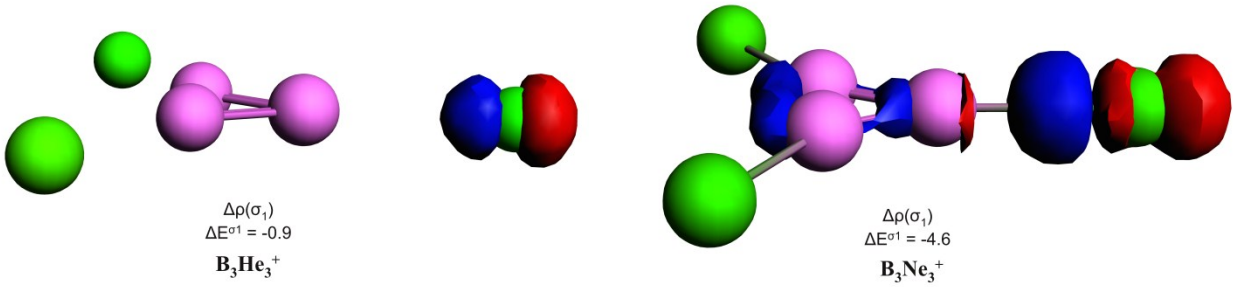

Fig. 2-SI. Plots of deformation densities, Δρ(**r**), of the pair-wise orbital interactions in of $B_3Ng_3^+$ (Ng = He, Ne) clusters at the revPBE-D3/TZ2P//MP2/def2-TZVP level. The associated orbital interaction energies are given in kcal/mol. The colour code of the charge flow is red→blue.

Table 1-SI. Average ZPE corrected dissociation energy (D_0, kcal/mol) of Ng-B bond, for the dissociation process: $B_3Ng_3^+ \longrightarrow B_3Ng_2^+ + 3Ng$, Ng-B and B-B bond distances (r, Å) in $B_3Ng_3^+$ at the CCSD(T)/def2-TZVP and MP2/def2-TZVP level, deviation (%) in bond length from the CCSD(T)/def2-TZVP.

$B_3Ng_3^+$	$D_0^{C\,a}$	D_0^{M}	$r_{Ng\text{-}B}^{C}$	$r_{Ng\text{-}B}^{M}$	$\%dev_{Ng\text{-}B}^{a}$	$r_{B\text{-}B}^{C}$	$r_{B\text{-}B}^{M}$	$\%dev_{B\text{-}B}^{b}$
						1.598	1.603	0.314
He	0.1	0.1	2.751	2.728	0.8	1.596	1.601	0.313
Ne	0.9	1.1	2.464	2.348	4.7	1.590	1.590	0.000
Ar	12.9 (13.0[c])	15.1	2.011	1.979	1.6	1.552	1.540	0.773
Kr	18.6	21.5	2.123	2.092	1.5	1.553	1.551	0.102
Xe	25.9	29.5	2.272	2.240	1.4	1.556	1.555	0.064
Rn	30.6	34.8	2.354	2.319	1.5	1.558	1.557	0.064

In the superscript 'C' and M stands for the CCSD(T) and MP2 level respectively; [a] the ZPE correction is taken from the MP2 level; [b] $\%dev = \frac{r^C - r^M}{r^C} \times 100$; [c] for only $B_3Ar_3^+$ complex the ZPE correction at the CCSD(T) level is included.

Table 2-SI. ZPE corrected dissociation energy (D_0, kcal/mol) of Ng-B bonds, enthalpy change (ΔH, kcal/mol), and free energy change (ΔG, kcal/mol) at 298 K for the dissociation process $B_3Ng_3^+ \longrightarrow B_3Ng_2^+ + 3Ng$ at the MP2/def2-TZVP, MP2/def2-QZVP and MP2/CBS levels, HOMO-LUMO energy gap (ΔE_{H-L}, eV) , NPA charge at B and Ng centres (q, au), Wiberg bond indices of Ng-B and B-B bonds (WBI), Ng-B and B-B bond distances (r, Å) in $B_3Ng_3^+$ at the MP2/def2-TZVP level.

Complex	D_0[a]	ΔH	ΔG	ΔE_{H-L}	q_B	q_{Ng}	WBI_{Ng-B}	WBI_{B-B}	r_{Ng-B}	r_{B-B}	r_{B-Ng}^{cov} [b]
$B_3He_3^+$	(0.4) {0.5} [0.6]	(0.1) {0.3} [0.4]	(-10.6) {-11.7} [-11.9]	8.62	0.32	0.01	0.02	1.56	2.728	1.601	1.120
B_3Ne_3	(3.4) {3.4} [3.4]	(3.3) {3.4} [3.4]	(-12.1) {-12.8} [-12.8]	9.17	0.30	0.04	0.06	1.56	2.348	1.590	1.420

[a]values in first, second and third braces represents results at the MP2/def2-TZVP, MP2/def2-QZVP and MP2/CBS levels respectively. [b] r_{B-Ng}^{cov} is calculated by taking summation of the covalent radii given in reference 36.

Table 3-SI. ZPE corrected successive dissociation energy (D_0^{BSSE}, kcal/mol) of M-Ng bonds, enthalpy change (ΔH, kcal/mol) at 298 K, free energy change (ΔG, kcal/mol) for the respective dissociation process at 298 K, NPA charges on B and Ng centres (q, au), Wiberg bond indices of Ng-B (WBI) of their respective mother moiety at the MP2/def2-TZVP level.

Ng	$B_3Ng_3^+$ [a] $\longrightarrow B_3Ng_2^+ + Ng$			$B_3Ng_2^+ \longrightarrow B_3Ng^+ + Ng$						$B_3Ng^+ \longrightarrow B_3^+ + Ng$					
	D_0^1	ΔH^1	ΔG^1	D_0^2	ΔH^2	ΔG^2	q_B[b]	q_{Ng}	WBI	D_0^3	ΔH^3	ΔG^3	q_B[b]	q_{Ng}	WBI
He	0.1	0.0	-4.1	0.0	0.0	-3.5	0.32	0.01	0.02	0.0	0.0	-2.9	0.32	0.01	0.02
Ne	0.4	1.0	-4.7	0.5	1.1	-3.0	0.28	0.05	0.08	-0.2	1.3	-4.5	0.22	0.11	0.01

[a]for the NPA charges on B and Ng centres (q, au), Wiberg bond indices of Ng-B (WBI) of $B_3Ng_3^+$ see Table 2; [b]q_B is the charge of that boron atom which is bonded to Ng-atom; The superscript 1, 2 and 3 denote the first, second and third dissociation process.

Table 4-SI. Electron density descriptors (au) at the bond critical points (r_c) in between Ng and B atoms in $B_3Ng_3^+$ (Ng = He, Ne) obtained from the wave functions generated at the MP2/def2-TZVP/WTBS//MP2/def2-TZVP level. (All electron WTBS basis set is used only for Xe and Rn).

Complex	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$G(r_c)$	$V\rho(r_c)$	$H(r_c)$
$B_3He_3^+$	0.004	0.016	0.003	-0.002	0.001
$B_3Ne_3^+$	0.016	0.048	0.012	-0.012	0.000

Table 5-SI. EDA results of the $B_3Ng_3^+$ (Ng = He, Ne) complexes considering Ng as one fragment and $B_3Ng_2^+$ as another fragment at the revPBE-D3/TZ2P// MP2/def2-TZVP level. All energy terms are in kcal/mol.

Complexs	ΔE^{Pauli}	ΔE^{elstat}	ΔE^{orb}	ΔE^{disp}	ΔE^{int}	ΔE^{σ}	ΔE^{rest}
$B_3He_3^+$	0.6	-0.1 (9.8)	-0.9 (64.3)	-0.4 (25.9)	-0.8	-0.9 (92.6)	-0.1
$B_3Ne_3^+$	5.9	-2.1 (25.9)	-5.6 (67.6)	-0.5 (6.4)	-2.4	-4.6 (83.3)	-0.9

Table 6-SI. The optimized structural parameters computed for $B_3Ng_2^+$ and B_3Ng^+ at the MP2/def2/TZVP level.

Ng	$B_3Ng_2^+$						B_3Ng^+					
	r_1	r_2	r_3	α	β	γ	r_1	r_2	r_3	α	β	γ
He	2.720	1.602	1.601	150.20	59.97	60.06	2.708	1.601	1.603	150.03	59.94	60.03
Ne	2.247	1.599	1.587	151.75	59.76	60.48	1.885	1.571	1.595	150.51	58.98	60.51
Ar	1.914	1.625	1.539	158.04	57.89	64.22	1.862	1.538	1.596	151.20	57.61	61.20
Kr	2.034	1.635	1.527	158.73	57.63	64.75	1.986	1.536	1.598	151.29	57.42	61.29
Xe	2.188	1.647	1.525	159.78	57.33	65.34	2.143	1.534	1.601	151.38	57.25	61.38
Rn	2.269	1.650	1.527	159.84	57.30	65.40	2.225	1.534	1.602	151.40	57.19	61.40

Cartesian coordinates

		MP2/Def2-TZVP				CCSD(T)/Def2-TZVP		
B_3^+	B	0.00000000	0.92548600	0.00000000	B	0.00000000	0.92259500	0.00000000
	B	-0.80149400	-0.46274300	0.00000000	B	0.79899100	-0.46129800	0.00000000
	B	0.80149400	-0.46274300	0.00000000	B	-0.79899100	-0.46129800	0.00000000
$B_3He_3^+$	B	0.00000000	0.92425100	0.00000000	B	0.00000000	0.92163400	0.00000000
	B	-0.80042500	-0.46212500	0.00000000	B	0.79815800	-0.46081700	0.00000000
	B	0.80042500	-0.46212500	0.00000000	B	-0.79815800	-0.46081700	0.00000000
	He	3.16332800	-1.82634800	0.00000000	He	-3.18091800	-1.83650400	0.00000000
	He	0.00000000	3.65269700	0.00000000	He	0.00000000	3.67300800	0.00000000
	He	-3.16332800	-1.82634800	0.00000000	He	3.18091800	-1.83650400	0.00000000
$B_3Ne_3^+$	B	0.00000000	0.91792600	0.00000000	B	0.00000000	0.91807300	0.00000000
	B	-0.79494700	-0.45896300	0.00000000	B	0.79507400	-0.45903600	0.00000000
	B	0.79494700	-0.45896300	0.00000000	B	-0.79507400	-0.45903600	0.00000000
	Ne	2.82831500	-1.63292900	0.00000000	Ne	-2.92888900	-1.69099500	0.00000000
	Ne	0.00000000	3.26585700	0.00000000	Ne	0.00000000	3.38198900	0.00000000
	Ne	-2.82831500	-1.63292900	0.00000000	Ne	2.92888900	-1.69099500	0.00000000
$B_3Ar_3^+$	B	0.00000000	0.89417700	0.00000000	B	0.00000000	0.89584900	0.00000000
	B	0.77438000	-0.44708800	0.00000000	B	0.77582800	-0.44792500	0.00000000
	B	-0.77438000	-0.44708800	0.00000000	B	-0.77582800	-0.44792500	0.00000000
	Ar	-2.48860900	-1.43679900	0.00000000	Ar	-2.51736300	-1.45340000	0.00000000
	Ar	0.00000000	2.87359800	0.00000000	Ar	0.00000000	2.90680000	0.00000000
	Ar	2.48860900	-1.43679900	0.00000000	Ar	2.51736300	-1.45340000	0.00000000
$B_3Kr_3^+$	B	0.00000000	0.89559400	0.00000000	B	0.00000000	0.89638000	0.00000000
	B	-0.77560700	-0.44779700	0.00000000	B	0.77628800	-0.44819000	0.00000000
	B	0.77560700	-0.44779700	0.00000000	B	-0.77628800	-0.44819000	0.00000000
	Kr	2.58765300	-1.49398200	0.00000000	Kr	-2.61508200	-1.50981800	0.00000000
	Kr	-2.58765300	-1.49398200	0.00000000	Kr	2.61508200	-1.50981800	0.00000000
	Kr	0.00000000	2.98796400	0.00000000	Kr	0.00000000	3.01963700	0.00000000
$B_3Xe_3^+$	B	0.00000000	0.89787200	0.00000000	B	0.00000000	0.89817100	0.00000000
	B	0.77758000	-0.44893600	0.00000000	B	0.77783900	-0.44908500	0.00000000
	B	-0.77758000	-0.44893600	0.00000000	B	-0.77783900	-0.44908500	0.00000000
	Xe	-2.71751400	-1.56895800	0.00000000	Xe	-2.74575200	-1.58526000	0.00000000
	Xe	2.71751400	-1.56895800	0.00000000	Xe	2.74575200	-1.58526000	0.00000000
	Xe	0.00000000	3.13791500	0.00000000	Xe	0.00000000	3.17052100	0.00000000
$B_3Rn_3^+$	B	0.00000000	0.89903300	0.00000000	B	0.00000000	0.89939100	0.00000000
	B	0.77858500	-0.44951700	0.00000000	B	0.77889500	-0.44969500	0.00000000
	B	-0.77858500	-0.44951700	0.00000000	B	-0.77889500	-0.44969500	0.00000000
	Rn	-2.78650900	-1.60879200	0.00000000	Rn	-2.81733800	-1.62659100	0.00000000
	Rn	2.78650900	-1.60879200	0.00000000	Rn	2.81733800	-1.62659100	0.00000000
	Rn	0.00000000	3.21758400	0.00000000	Rn	0.00000000	3.25318200	0.00000000

Ng		$B_3Ng_2^+$				B_3Ng^+		
He	B	0.00000000	0.00000000	1.30914100	B	0.00000000	0.80058100	-0.89031300
	B	0.00000000	0.80124300	-0.07694300	B	0.00000000	-0.80058100	-0.89031300
	B	0.00000000	-0.80124300	-0.07694300	B	0.00000000	0.00000000	0.49810200
	He	0.00000000	-3.15289200	-1.44406800	He	0.00000000	0.00000000	3.20631000

	He	0.00000000	3.15289200	-1.44406800				
Ne	B	0.00000000	0.79939600	0.47513000	B	0.00000000	0.78533400	-1.58717400
	B	0.00000000	-0.79939600	0.47513000	B	0.00000000	0.00000000	-0.19842700
	B	0.00000000	0.00000000	1.84630400	B	0.00000000	-0.78533400	-1.58717400
	Ne	0.00000000	2.71485900	-0.69914100	Ne	0.00000000	0.00000000	1.68638700
	Ne	0.00000000	-2.71485900	-0.69914100				
Ar	B	0.00000000	0.00000000	1.96078500	B	0.00000000	0.76913200	-1.99063500
	B	0.00000000	0.81246100	0.66599100	B	0.00000000	0.00000000	-0.59185200
	B	0.00000000	-0.81246100	0.66599100	B	0.00000000	-0.76913200	-1.99063500
	Ar	0.00000000	-2.36242000	-0.45732900	Ar	0.00000000	0.00000000	1.27031200
	Ar	0.00000000	2.36242000	-0.45732900				
Kr	B	0.00000000	0.00000000	2.21293600	B	0.00000000	0.76782500	-2.52859800
	B	0.00000000	0.81737700	0.92365200	B	0.00000000	-0.76782500	-2.52859800
	B	0.00000000	-0.81737700	0.92365200	B	0.00000000	0.00000000	-1.12674800
	Kr	0.00000000	-2.45522700	-0.28196100	Kr	0.00000000	0.00000000	0.85888100
	Kr	0.00000000	2.45522700	-0.28196100				
Xe	B	0.00000000	0.82350300	1.10706600	B	0.00000000	0.76684500	-2.87892600
	B	0.00000000	-0.82350300	1.10706600	B	0.00000000	0.00000000	-1.47387300
	B	0.00000000	0.00000000	2.39116200	B	0.00000000	-0.76684500	-2.87892600
	Xe	0.00000000	-2.56872600	-0.21320800	Xe	0.00000000	0.00000000	0.66960400
	Xe	0.00000000	2.56872600	-0.21320800				
Rn	B	0.00000000	0.82493800	1.22595000	B	0.00000000	0.76690900	-3.16179000
	B	0.00000000	-0.82493800	1.22595000	B	0.00000000	0.00000000	-1.75493400
	B	0.00000000	0.00000000	2.51098700	B	0.00000000	-0.76690900	-3.16179000
	Rn	0.00000000	-2.63385000	-0.14427000	Rn	0.00000000	0.00000000	0.46968100
	Rn	0.00000000	2.63385000	-0.14427000				