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A computational study to determine whether substituents make $E_{13}{\equiv}$nitrogen (E_{13} = B, Al, Ga, In, and Tl) triple bonds synthetically accessible†

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This study theoretically determines the effect of substituents on the stability of the triple-bonded L–$E_{13}{\equiv}$N–L (E_{13} = B, Al, Ga, In, and Tl) compound using the M06-2X/Def2-TZVP, B3PW91/Def2-TZVP, and B3LYP/LANL2DZ+dp levels of theory. Five small substituents (F, OH, H, CH_3 and SiH_3) and four large substituents (SiMe(Si*t*Bu$_3$)$_2$, Si*i*PrDis$_2$, Tbt (= C_6H_2-2,4,6-{CH($SiMe_3$)$_2$}$_3$) and Ar* (=C_6H_3-2,6-(C_6H_2-2,4,6-i-Pr_3)$_2$)) are used. Unlike other triply bonded L–$E_{13}{\equiv}$P–L, L–$E_{13}{\equiv}$As–L, L–$E_{13}{\equiv}$Sb–L and L–$E_{13}{\equiv}$Bi–L molecules that have been studied, the theoretical findings for this study show that both small (but electropositive) ligands and bulky substituents can effectively stabilize the central $E_{13}{\equiv}$N triple bond. Nevertheless, these theoretical observations using the natural bond orbital and the natural resonance theory show that the central $E_{13}{\equiv}$N triple bond in these acetylene analogues must be weak, since these $E_{13}{\equiv}$N compounds with various ligands do not have a real triple bond.

1. Introduction

Molecules that feature multiple bonds have been the subject of many studies because of their economic and academic importance.[1–49] Recently, molecules containing a L–$E_{13}{\equiv}E_{15}$–L (E_{13} = B, Al, Ga, In, and Tl; E_{15} = P, As, Sb, and Bi) triple bond, which are isoelectronic to the alkyne analogues R–$E_{14}{\equiv}E_{14}$–R (E_{14} = C, Si, Ge, Sn and Pb), have been the subject of theoretical study.[52–65] This study focuses on the other acetylene analogues; *i.e.*, the triply bonded L–$E_{13}{\equiv}$N–L compounds that contain group 13 (E_{13}) and nitrogen atoms. As far as the authors are aware, only very few triply bonded compounds that contain a nitrogen element (*i.e.*, L–B≡N–L,[66–69] L–Ga≡N–L,[70,71] and L–In≡N–L[70]) have been successfully synthesized and isolated. No other triple bond molecules containing aluminum (L–Al≡N–L) and thallium (L–Tl≡N–L) have been both experimentally and theoretically reported.

Although the authors have already published 14 papers concerning group 13 group 15 triple bond molecules,[52–65] the present computational evidence demonstrates that the results about the stability of the triply bonded $RE_{13}{\equiv}$NR compounds are quite different from our previous theoretical examinations. For instance, the theoretical conclusions based on our previous papers show that only the bulky ligands can stabilize the triply bonded L–$E_{13}{\equiv}E_{15}$–L (E_{15} = P, As, Sb, and Bi) molecules.[52–65] Nevertheless, in this work, the authors' computations in this work reveal that both small (but electropositive) ligands and bulky substituents can effectively stabilize the triply bonded L–$E_{13}{\equiv}$N–L compounds. In other words, the present theoretical evidences emphasize that both small (but electropositive) substituents and sterically bulky groups can successfully protect the central triple bond, which, in turn, can increase the bond order of this triple bond. Because of the difficulties in experimentally synthesizing these rare triply bonded molecules, this study theoretically determines the effect of substituents on the formation of L–$E_{13}{\equiv}$N–L featuring a triple bond. The geometrical structures and associated properties of stable L–$E_{13}{\equiv}$N–L molecules are theoretically predicted. Accordingly, the present work can conduct the experimental chemists how to design and synthesize the triply bonded $RE_{13}{\equiv}$NR compounds using the effective way.

2. General considerations

In order to determine the valence electronic structures of L–$E_{13}{\equiv}$N–L, similarly to our previous studies,[50–64] the L–$E_{13}{\equiv}$N–L species is divided into two fragments: L–E_{13} and L–N. These are shown in Fig. 1.

As seen in Fig. 1, there are two mechanisms for the formation of the L–$E_{13}{\equiv}$N–L triple bond species at the singlet ground state. The choice of mechanism [A] or mechanism [B] respectively depends on the promotion energy of L–N and L–E_{13} moieties. For mechanism [A], a singlet L–E_{13} and a singlet L–N combine to yield a singlet L–$E_{13}{\equiv}$N–L molecule, which is named a singlet–singlet bonding ($[\text{L–E}_{13}]^1 + [\text{L–N}]^1 \rightarrow [\text{L–E}_{13}{\equiv}\text{N–L}]^1$). For mechanism [B], a triplet L–E_{13} and a triplet L–N

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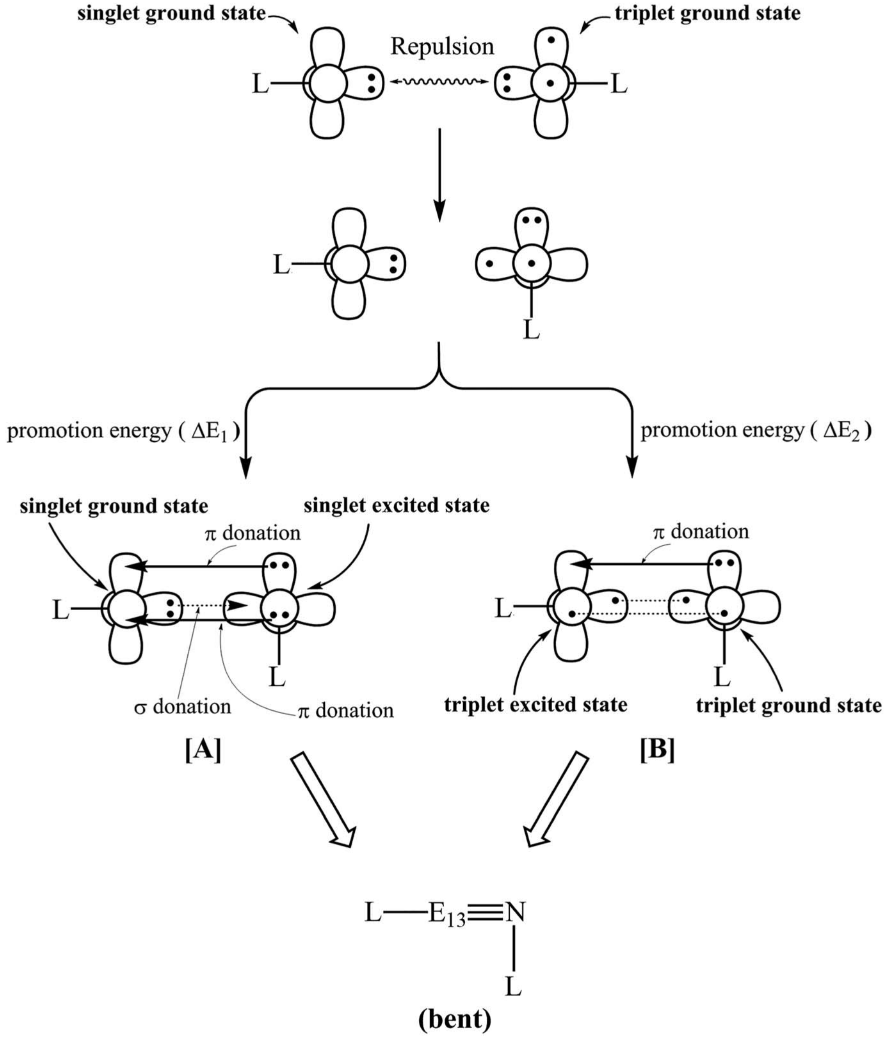


Fig. 1 The valence-bond bonding mechanisms [A] and [B] for the triply bonded $L{-}E_{13}{\equiv}N{-}L$ molecule: $\Delta E_1 = E$(triplet state for R–N) − E(singlet state for R–N) and $\Delta E_2 = E$(triplet state for $R{-}E_{13}$) − E(singlet state for $R{-}E_{13}$).

couple to yield a singlet $L{-}E_{13}{\equiv}N{-}L$ compound, which is called a triplet–triplet bonding ($[L{-}E_{13}]^3 + [L{-}N]^3 \rightarrow [L{-}E_{13}{\equiv}N{-}L]^1$).

The chemical bonding nature of mechanism [A] in Fig. 1 contains three types of chemical bonds: a valence lone pair orbital of E_{13} → a valence p orbital of N, a valence p orbital of E_{13} ← a valence lone pair orbital of N, and a valence p orbital of E_{13} ← a valence p orbital of N. In other words, the $E_{13}{\equiv}N$ triple bond features one $E_{13} \rightarrow N$ σ donation bond and two $E_{13} \leftarrow N$ π donation bonds. Therefore, the central $E_{13}{\equiv}N$ triple bond in mechanism [A] can be regarded as $L{-}E_{13}\overset{\longleftarrow}{\underset{\longrightarrow}{\longleftarrow}}N{-}L$.

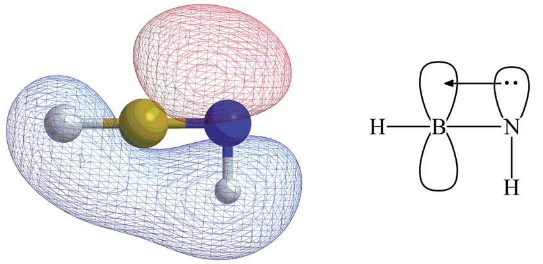
For mechanism [B], the chemical bonding character of the $E_{13}{\equiv}N$ triple bond in Fig. 1 involves three types of chemical bonds: a valence lone pair orbital of E_{13} — a valence p orbital of N, a valence p orbital of E_{13} — a valence p orbital of N, and a valence p orbital of E_{13} ← a valence lone pair orbital of N. The $E_{13}{\equiv}N$ triple bond features one traditional $E_{13}{-}N$ σ bond, one traditional $E_{13}{-}N$ π bond and one $E_{13} \leftarrow N$ π donation bond. Therefore, the principal $E_{13}{\equiv}N$ triple bond in mechanism [B] can be described as $L{-}E_{13}\overset{\longleftarrow}{=}N{-}L$. The two non-degenerate π bonding orbitals ($\pi_\perp$ and $\pi_\parallel$) for $H{-}B{\equiv}N{-}H$ are schematically represented in Fig. 2.

It is noteworthy that, as demonstrated in Fig. 1, the vital bonding in the triply bonded $L{-}E_{13}{\equiv}N{-}L$ species contributes greatly to the lone pair of the N–L moiety, whose electron pair is donated to the empty p–π orbital of the $L{-}E_{13}$ component. In particular, the lone pair orbital of the N–L unit includes the s valence orbital of nitrogen. The atomic size of E_{13} is also apparently different from that of nitrogen, especially for the E_{13} elements with a higher atomic number. Therefore, the overlap in the orbital populations between E_{13} and nitrogen is expected to be small. That is to say, from the overlap population viewpoint, this theoretical analysis anticipates that the triple bond between E_{13} and N must be weak. This prediction is verified in the following discussion.

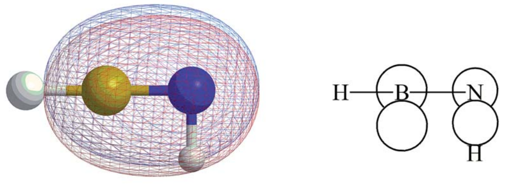
3. Results and discussion

3.1 Small ligands on substituted $L{-}E_{13}{\equiv}N{-}L$

The effect of small ligands L (=F, OH, H, CH_3 and SiH_3) on the stability of the triply bonded $L{-}B{\equiv}N{-}L$ molecules is determined. For comparison, three computational methods (M06-2X/Def2-TZVP, B3PW91/Def2-TZVP, and B3LYP/LANL2DZ+dp),



(a) $\pi_\perp$



(b) $\pi_{//}$

Fig. 2 The natural B≡N π bonding orbitals ($\pi_\perp$ and $\pi_\parallel$ for (a) and (b), respectively) for H–B≡N–H, based on Fig. 1.

based on density functional theory (DFT), are used to determine the relative stability of the doubly bonded L_2B=N: and :B=NL_2 and the triply bonded L–B≡N–L. The calculated potential energy surfaces are schematically shown in Fig. 3.

Interestingly, unlike the other L–E_{13}≡E_{15}–L molecular systems that have been previously studied,[50–64] the theoretical data for this study using three DFT methods suggest that when ligands are small and electropositive, the triply bonded L–B≡N–L molecule could be experimentally produced and detected, since these triple bonded species are more thermodynamically stable than their corresponding doubly bonded L_2B=N: and :B=NR_2 isomers. Actually, these triply bonded L–B≡N–L species, which is isoelectronic to the alkynes L–C≡C–L and which contain small and electropositive substituents were experimentally isolated and structurally characterized about three decades ago.[65–68]

Several important geometrical parameters and the associated physical properties of L–B≡N–L (Table 1), L–Al≡N–L (Table S1†), L–Ga≡N–L (Table S2†), L–In≡N–L (Table S3†) and L–Tl≡N–L (Table S4†) are listed in ESI.†

As shown in Table 1, these computations predict that the B≡N triple bond distance (Å) lies in the range, 1.246–1.276 (B3PW91/Def2-TZVP), 1.233–1.254 (M06-2X/Def2-TZVP) and 1.220–1.248 (B3LYP/LANL2DZ+dp). The reported experimental values for the B≡N triple bond length are 1.240 Å (ref. 65 and 66) and 1.258 Å,[67,68] which agree well with the theoretical data for this study.

In the case of the ΔE_{ST} (=E(triplet state) − E(singlet state)) for the L–B fragment (Table 1), its excited energy from the singlet ground state to the triplet excited state is theoretically estimated to be at least 22 kcal mol^{-1}. However, for the L–N moiety, the modulus advancement energy between the ground state and the first excited state is calculated to be at least 20 kcal mol^{-1}. On the basis of the theoretical analysis in Section 2, this theoretical data shows that mechanism [A] is feasible for the interpretation of the generation of the triply bonded L–B≡N–L species that feature small ligands. Therefore, the bonding disposition of L–B≡N–L with small substituents must be viewed as L–B$\underset{\rightarrow}{\leftleftarrows}$N–L, so one B → N σ donation bond and two B ← N π donation bonds constitute the B≡N triple bond. All the values for the Wiberg bond index (WBI)[71,72] in Table 1 show that B≡N bonds that are supported by small groups have values of less than 2.1, but the WBI for the C≡C bond in ethyne is 2.99. These L–B≡N–L species that feature small substituents have a bond order of much less than 2.00 for the central B–N bond, as shown in Table 1. One explanation for this is that, as shown in Fig. 1, the lone pair orbitals of both the L–B and L–N components contain the valence s characters. This significantly decreases the bonding strength between boron and nitrogen. It is also possible that the covalent radii of boron and nitrogen, at 82 pm and 70 pm,[73] result in a small overlapping population between B and N, which could result in small WBI values.

Similar to the 1,2-migration reactions for L–B≡N–L, the potential energy surfaces for the other triply bonded L–Al≡N–L, L–Ga≡N–L, L–In≡N–L and L–Tl≡N–L compounds are schematically represented in Fig. 4–7, respectively. Being close to the L–B≡N–L (Fig. 3) compound, the computational results for the 1,2-ligand-shift reactions show that either a proton or the ligands containing the carbon atom (such as CH_3) stabilize the triply bonded L–E_{13}≡N–L (E_{13} = Al, Ga, In and Tl) species relative to their corresponding double-bond isomers. This theoretical finding is quite different from those for the other L–E_{13}≡E_{15}–L systems that have been previously studied,[52–64] in which regardless of whether the small ligands are electronegative or electropositive, the triple-bond L–E_{13}≡E_{15}–L (except for E_{15} = N) compounds are not thermodynamically stable in the 1,2-migration reactions. To the authors' best knowledge, both monomeric imides Ar′–M≡N–Ar″ (M = Ga or In; Ar′ or Ar″ = terphenyl ligands) that were reported by Power and co-workers have been successfully synthesized and structurally characterized.[69,70] The computed geometrical parameters and some physical properties of the L–E_{13}≡N–L (E_{13} = Al, Ga, In and Tl) molecules featuring small groups are listed in Tables S1, S2, S3, and S4,† respectively. Several important conclusions can be drawn from Tables S1–S4.†

(1) It is noteworthy that according to the available experimental detections, the lengths of the Ga≡N (1.701 Å)[69,70] and In≡N (1.928 Å)[69] triple bonds are consistent with the computational results (1.662–1.804 Å and 1.828–2.073 Å) in Tables S2 and S3,† respectively. This theoretical evidence strongly suggests that the computational methods that are used in this study provide reliable information for further theoretical observations.

(2) The results using DFT that are shown in Table S1† (L–Al≡N–L) and Table S4† (L–Tl≡N–L) predict that the central Al≡N and Tl≡N bond distances are in the range, 1.608–1.753 Å and 1.849–2.300 Å, respectively. The calculated WBI for the central Al–N, Ga–N, In–N, and Tl–N bonds are all estimated to be less than 1.50. This theoretical evidence strongly suggests that all of these central triple bonds in L–E_{13}≡N–L molecules that feature small substituents must be quite weak, possibly because of the hybridized lone pair orbitals for both L–E_{13} and

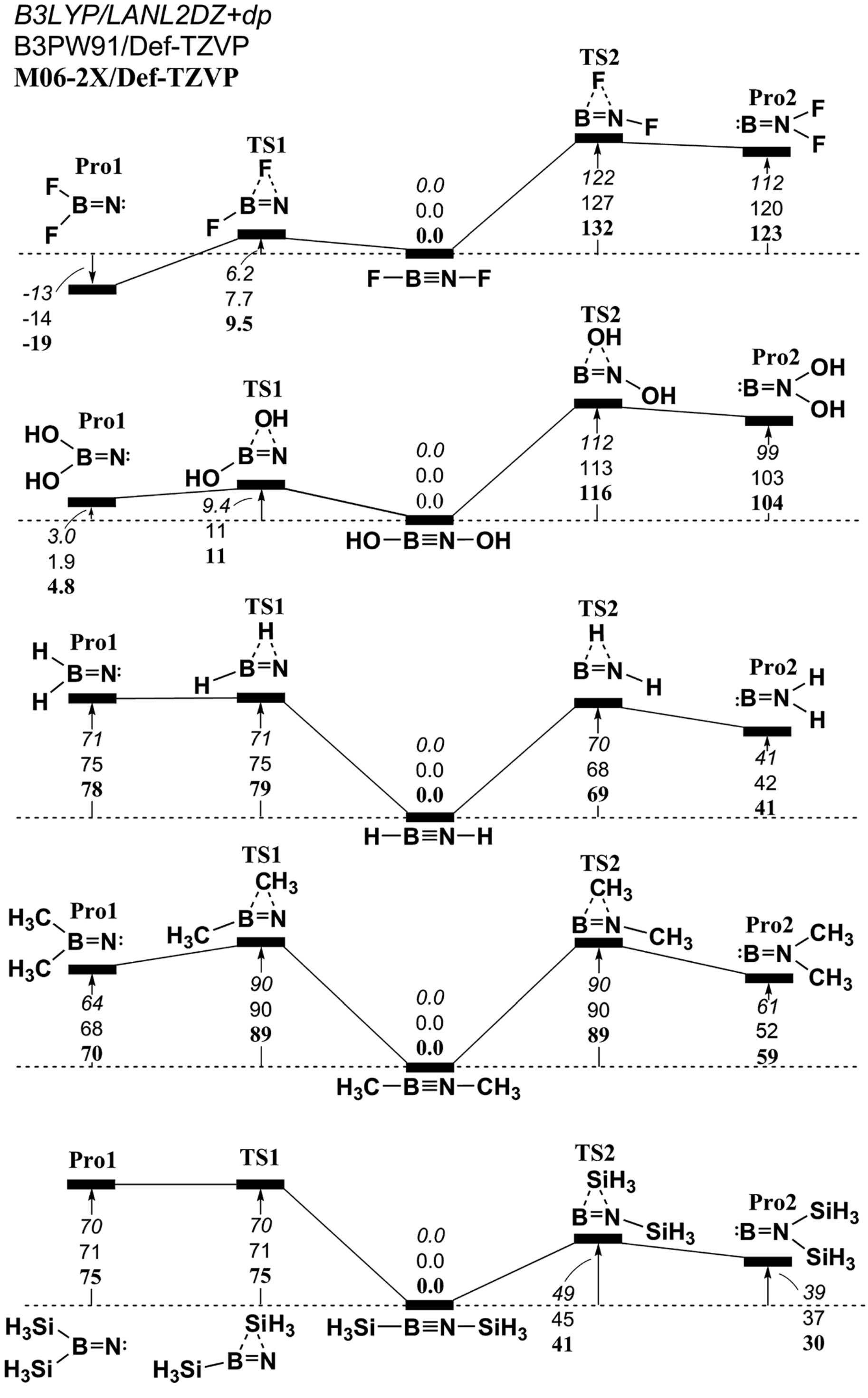


Fig. 3 The relative Gibbs free energy for L–B≡N–L (L = F, OH, H, CH_3, and SiH_3) calculated at the M06-2X/Def2-TZVP, B3PW91/Def2-TZVP, and B3LYP/LANL2DZ+dp levels of theory. For details see the text and Table 1.

L–N fragments and the different atomic radius for E_{13} and N elements, both of which do not produce good overlap populations between nitrogen and the group 13 elements.

(3) The DFT data in Tables S1–S4† shows that the singlet–triplet energy splitting (ΔE_{ST}) for the L–E_{13} fragment is much higher than that for the L–N moiety. Therefore, the electron for the latter jumps from the triplet ground state to the singlet excited state more easily than the electron from the singlet ground state for the former. As a result, it is better to use mechanism [A] to describe the bonding characteristic of the L–E_{13}≡N–L molecule bearing the small substituents. For mechanism [A] in Fig. 1, the bonding constitution for the E_{13}≡N

Table 1 The important geometrical parameters, the Wiberg bond index (WBI), the natural charge densities (Q_B and Q_N), the HOMO–LUMO energy gaps, the singlet–triplet energy splitting (ΔE_B and ΔE_N), and the binding energies (BE) for $L{-}B{\equiv}N{-}L$ using the B3PW91/Def2-TZVP, M06-2X/Def2-TZVP (in round bracket), and B3LYP/LANL2DZ+dp (in square bracket) levels of theory

L	F	OH	H	CH_3	SiH_3
$B{\equiv}N$ (Å)	1.275	1.276	1.246	1.249	1.262
	(1.245)	(1.254)	(1.233)	(1.239)	(1.252)
	[1.220]	[1.238]	[1.231]	[1.236]	[1.248]
$\angle$L–B–N (°)	165.4	169.1	180.0	180.0	180.0
	(169.1)	(170.7)	(180.0)	(180.0)	(180.0)
	[180.0]	[174.1]	[179.9]	[179.9]	[178.6]
$\angle$B–N–L (°)	137.3	137.0	180.0	180.0	180.0
	(151.4)	(146.5)	(180.0)	(180.0)	(179.9)
	[160.0]	[158.2]	[179.9]	[179.9]	[178.9]
$\angle$L–B–N–L (°)	180.0	163.5	163.0	180.0	169.1
	(179.9)	(161.9)	(169.3)	(178.7)	(176.9)
	[180.0]	[159.7]	[178.8]	[178.4]	[172.1]
Q_B[a]	0.2569	0.0441	0.1196	−0.1350	−0.2670
	(0.1543)	(−0.0515)	(−0.1194)	(−0.2172)	(−0.1986)
	[0.1335]	[−0.0465]	[−0.0817]	[−0.2570]	[−0.2213]
Q_N[b]	0.1573	0.1411	−0.2376	−0.1295	−0.0263
	(0.2340)	(0.1185)	(−0.2197)	(−0.1512)	(−0.0584)
	[0.2253]	[0.1226]	[−0.2575]	[−0.1150]	[−0.0537]
ΔE_{ST} for L–B[c] (kcal mol^{-1})	73.97	64.90	25.39	36.79	22.28
	(73.60)	(62.12)	(27.65)	(32.69)	(21.77)
	[81.01]	[68.97]	[28.74]	[38.47]	[22.33]
ΔE_{ST} for L–N[d] (kcal mol^{-1})	−46.00	−21.39	−50.89	46.76	44.87
	(−48.48)	(−21.68)	(−55.08)	(48.23)	(46.86)
	[−45.47]	[−19.91]	[−49.44]	[50.99]	[48.02]
HOMO–LUMO (kcal mol^{-1})	147.8	128.3	197.6	162.2	165.6
	(173.2)	(145.9)	(206.1)	(182.3)	(165.4)
	[242.5]	[203.2]	[265.7]	[228.3]	[224.4]
BE[e] (kcal mol^{-1})	149.7	168.2	200.1	188.8	206.2
	(147.5)	(166.1)	(202.4)	(190.3)	(208.4)
	[157.4]	[171.4]	[210.5]	[199.4]	[217.4]
WBI[f]	1.880	1.843	2.114	1.962	1.908
	(1.951)	(1.911)	(2.149)	(2.000)	(1.963)
	[1.988]	[1.938]	[2.128]	[2.000]	[1.960]

[a] The natural charge density on B. [b] The natural charge density on N. [c] $\Delta E_{ST} = E$(triplet state for L–B) − E(singlet state for L–B). [d] $\Delta E_{ST} = E$(triplet state for L–N) − E(singlet state for L–N). [e] BE = E(singlet state for L–B) + E(singlet state for L–B) – E(singlet state for $L{-}B{\equiv}N{-}L$). [f] The Wiberg bond index (WBI) for the $B{\equiv}N$ bond: see ref. 71 and 72.

triple bond in $L{-}E_{13}{\equiv}N{-}L$ that feature small ligands must be $L{-}E_{13}\leftrightarrows N{-}L$.

3.2 Large ligands on substituted $L'{-}E_{13}{\equiv}N{-}L'$

The possibility of bulky substituents (L′) stabilizing the central $E_{13}{\equiv}N$ triple bond is determined. Similarly to previous studies,[52–64] as shown in Scheme 1, SiMe(Si*t*Bu$_3$)$_2$, Si*i*PrDis$_2$, Tbt and Ar* are used for this study. London dispersion forces, which are the non-valent interactions between large groups, can greatly affect the structure and stability of sterically congested molecules.[74] Therefore, the dispersion-corrected M06-2X/Def2-TZVP method[75] is used to gain more information about producing stable, triple-bonded $L'{-}E_{13}{\equiv}N{-}L'$ species. The key geometrical parameters and the associated physical properties of $L'{-}B{\equiv}N{-}L'$ are listed in Table 2. This information for other triply bonded molecules that feature bulky ligands, *i.e.*, $L'{-}Al{\equiv}N{-}L'$ (Table S5†), $L'{-}Ga{\equiv}N{-}L'$ (Table S6†), $L'{-}In{\equiv}N{-}L'$ (Table S7†), and $L'{-}Tl{\equiv}N{-}L'$ (Table S8†), is collected in ESI.†

The same computational method is used to determine the 1,2-ligand-shift reactions for $L'{-}E_{13}{\equiv}N{-}L'$ molecules that are substituted with bulky groups; *i.e.*, $L'{-}E_{13}{\equiv}N{-}L' \rightarrow L_2'E_{13}{\equiv}N{:}$ and $L'{-}E_{13}{\equiv}N{-}L' \rightarrow {:}E_{13}{=}NL_2'$, as shown in Scheme 2. The results in Table 2 show that because of steric crowding, the potential energies of both double-bond molecules (${:}B{=}NL_2'$ and $L_2'B{=}N$) are respectively higher than that of the corresponding triple-bond $L'{-}B{\equiv}N{-}L'$ isomer by at least 80 and 71 kcal mol^{-1}. These theoretical findings strongly suggest that sterically hindered ligands shield the central weak $B{\equiv}N$ triple bond, since the Wiberg bond index (WBI) for the $C{\equiv}C$ bond in acetylene was computed to be 2.99.

The computational data in Tables 2 and S5–S8† shows that the central triple bond distances are predicted to be in the range of 1.242–1.273 Å ($L'{-}B{\equiv}N{-}L'$), 1.681–1.719 Å ($L'{-}Al{\equiv}N{-}L'$), 1.698–1.722 Å ($L'{-}Ga{\equiv}N{-}L'$), 1.866–1.902 Å ($L'{-}In{\equiv}N{-}L'$), and 1.877–1.930 Å ($L'{-}Tl{\equiv}N{-}L'$). These predicted bond lengths are consistent with other reported experimental data, such as, 1.240 Å (ref. 65 and 66) and 1.258 Å (ref. 67 and 68) for the $B{\equiv}N$ bond,

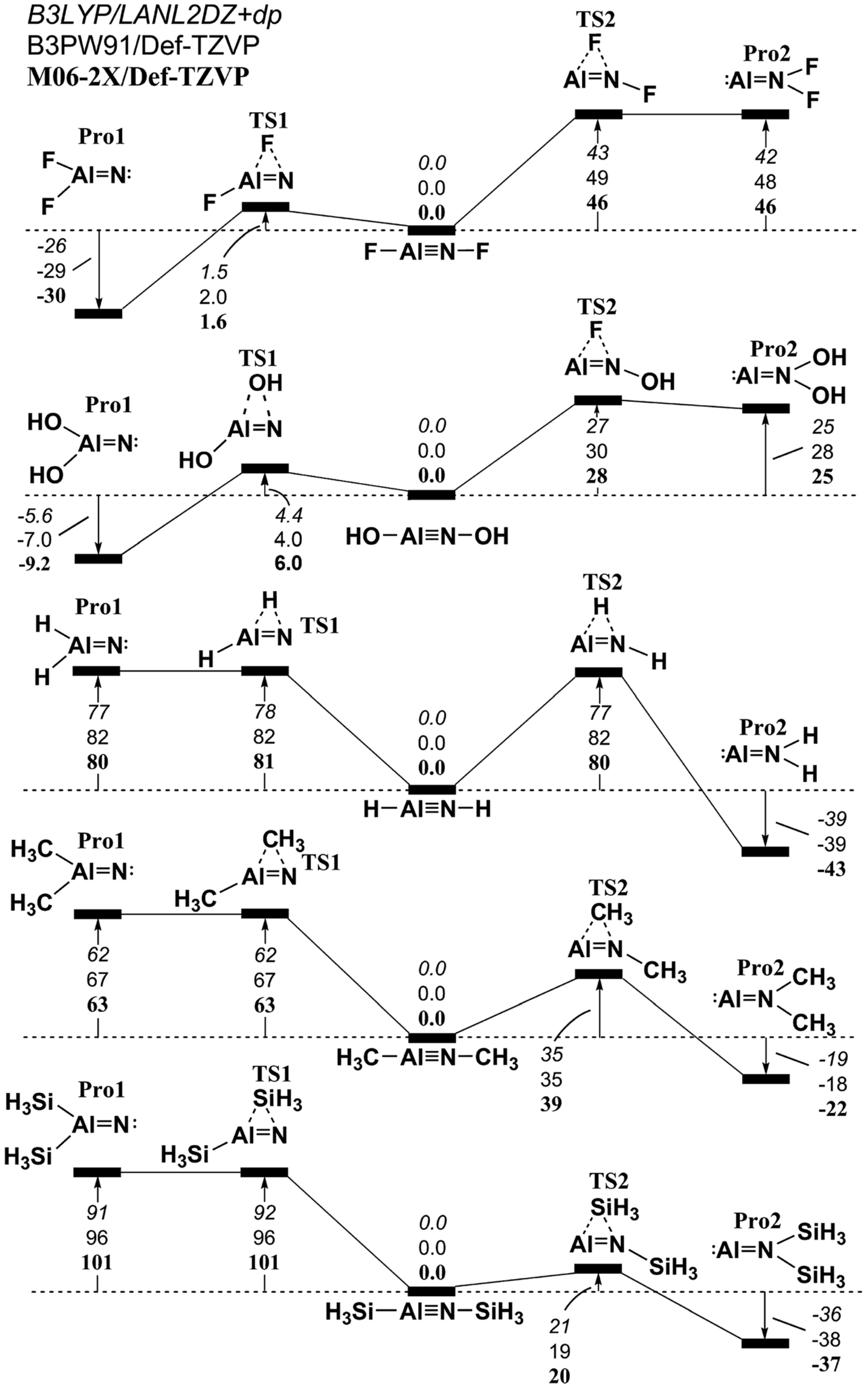


Fig. 4 The relative Gibbs free energy for L–Al≡N–L (L = F, OH, H, CH_3, and SiH_3) calculated at the M06-2X/Def2-TZVP, B3PW91/Def2-TZVP, and B3LYP/LANL2DZ+dp levels of theory. For details see the text and Table S1.†

1.701 Å (ref. 69 and 70) for the Ga≡N bond and 1.928 Å (ref. 69) for the In≡N bond. Since there is good agreement between the available experimental values and the dispersion-corrected M06-2X data for the central triple bond lengths, the computational method that is used in this study must be reliable.

The M06-2X results in Table 2 show that the $\Delta E'_{ST}$ for the L′–B fragment is calculated to be at least 11 kcal mol^{-1}, but the modulus of $\Delta E'_{ST}$ for the L′–N component is computed to be at least 22 kcal mol^{-1}. In other words, L′–B jumps easily from the singlet ground state to the triplet state because the

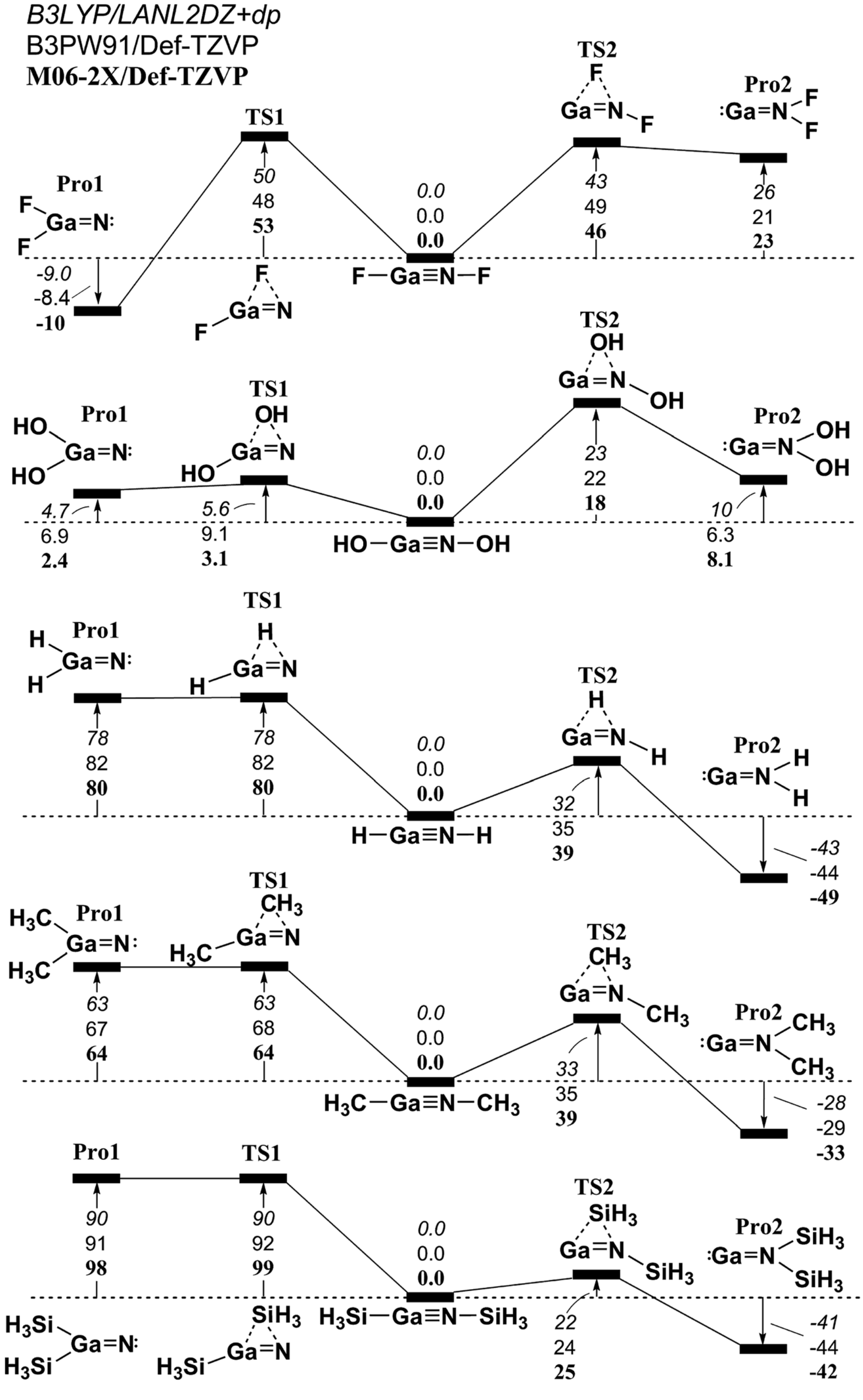


Fig. 5 The relative Gibbs free energy for L–Ga≡N–L (L = F, OH, H, CH_3, and SiH_3) calculated at the M06-2X/Def2-TZVP, B3PW91/Def2-TZVP, and B3LYP/LANL2DZ+dp levels of theory. For details see the text and Table S2.†

$\Delta E'_{ST}$ value for L′–B is smaller than that for L′–N. Therefore, the L′–B and L′–N fragments must follow a triplet–triplet bonding mechanism; *i.e.*, mechanism [B]: $[L'{-}B]^3 + [L'{-}N]^3 \rightarrow [L'{-}B{\equiv}N{-}L']^1$. As schematically shown in Fig. 1, the bonding nature of the bulkily substituted L′–B≡N–L′ can be viewed as $L'{-}B\overset{\longleftarrow}{=}N{-}L'$. That is to say, this B≡N triple bond consists of a usual σ bond, a conventional π bond and a donor–acceptor π bond.

However, each lone-pair orbital of L′–B and L′–N respectively contains s and p valence orbitals of boron and nitrogen. As shown in Fig. 1, this phenomenon means that the overlap population between L′–B and L′–N is small. Therefore, the bond

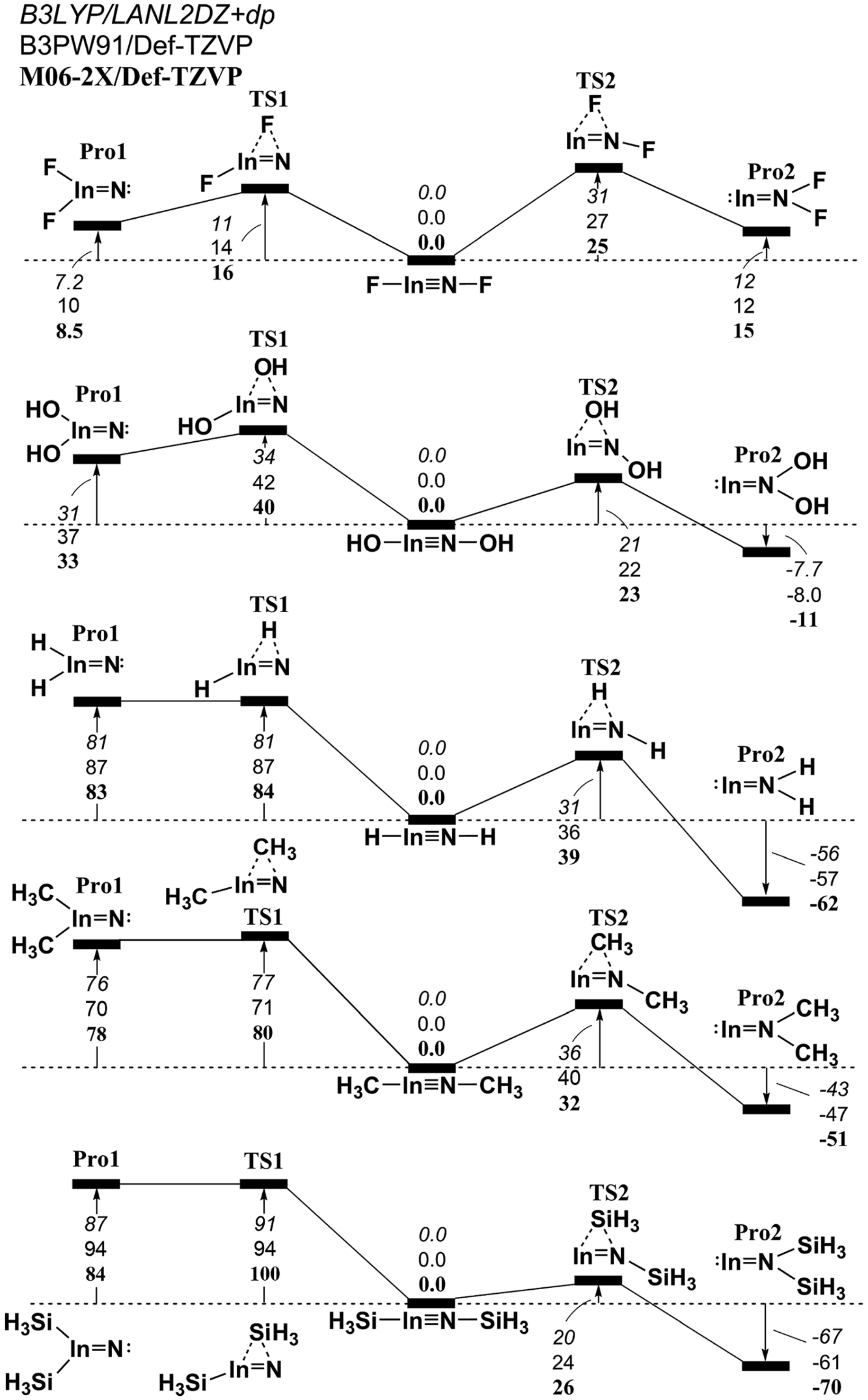


Fig. 6 The relative Gibbs free energy for L–In≡N–L (L = F, OH, H, CH_3, and SiH_3) calculated at the M06-2X/Def2-TZVP, B3PW91/Def2-TZVP, and B3LYP/LANL2DZ+dp levels of theory. For details see the text and Table S3.†

order for the B≡N triple bond must be small. This study's M06-2X computations are shown in Table 2 and confirm this prediction. Similarly, the values for $\Delta E'_{\mathrm{ST}}$ for L′–N and the other L′–B fragments in Tables S5–S8† show that the modulus of $\Delta E'_{\mathrm{ST}}$ (>22 kcal mol^{-1}) for the former is always larger than those for the latter, *e.g.*, L′–Al (>18 kcal mol^{-1}), L′–Ga (>15 kcal mol^{-1}), L′–In (>17 kcal mol^{-1}) and L′–Tl (>19 kcal mol^{-1}). These computational values show that all of the bonding in these triply bonded L′–E_{13}≡N–L′ species can be represented as L′–$E_{13}\overset{\longleftarrow}{\equiv}$N–L′.

The theoretically calculated values for the 1,2-shifted energy barriers and the B≡N bond orders (WBI) in Table 2 strongly

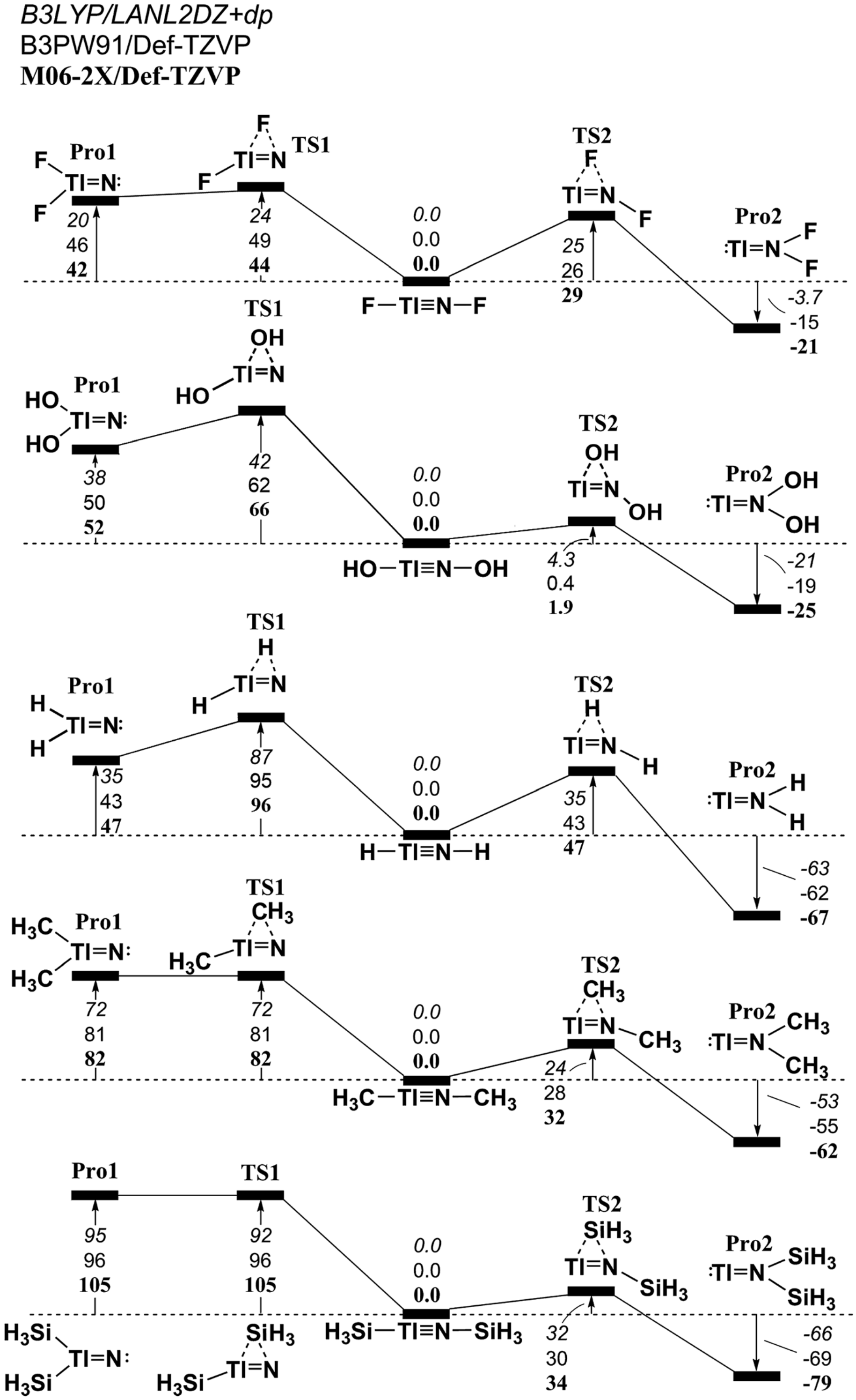
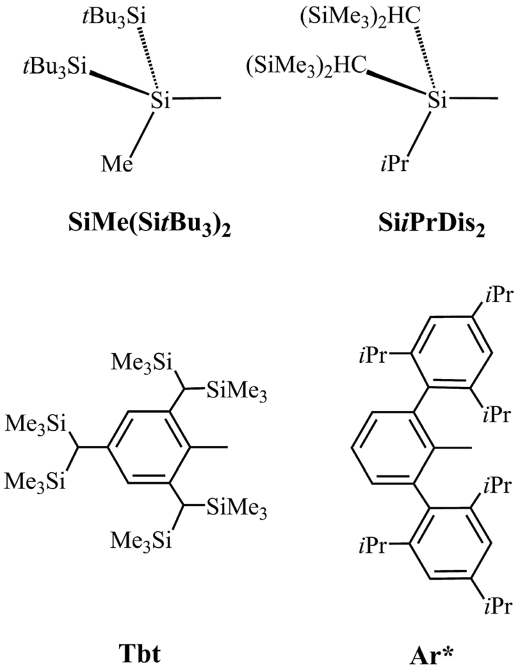


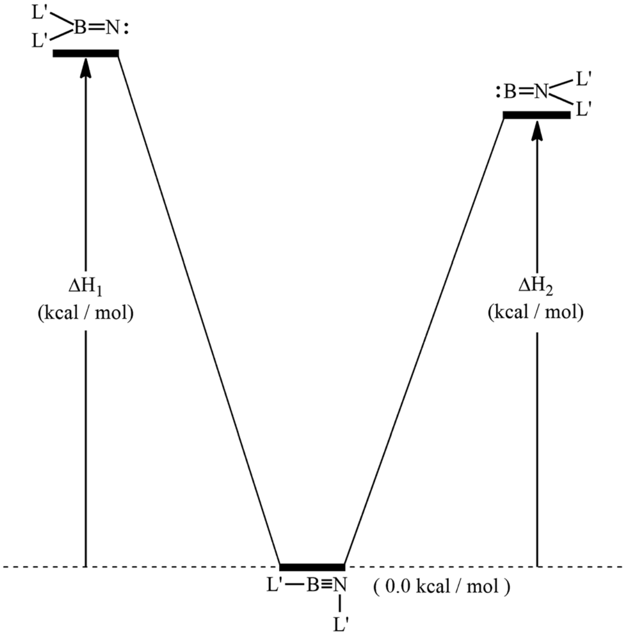
Fig. 7 The relative Gibbs free energy for L–Tl≡N–L (L = F, OH, H, CH_3, and SiH_3) calculated at the M06-2X/Def2-TZVP, B3PW91/Def2-TZVP, and B3LYP/LANL2DZ+dp levels of theory. For details see the text and Table S4.†

indicate that large substituents protect the central fragile B≡N triple bond and increase its bond order. The same conclusions can also be drawn from the computational results for the other triply bonded L′–E_{13}≡N–L′ molecules, which are listed in Tables S5–S8.†

Both natural bond orbital (NBO)[71,72] and natural resonance theory (NRT)[76–78] are used to determine the electronic densities of the triply bonded L′–B≡N–L′ molecules that feature large substituents. The M06-2X results are listed in Table 3. The same theoretical analysis for the other triply bonded L′–



Scheme 1



(L′ = SiMe(Si*t*Bu$_3$)$_2$, Si*i*PrDis$_2$, Ar*, and Tbt)

Scheme 2

$\mathrm{E_{13}}$≡N–L′ species is listed in ESI:† L′–Al≡N–L′ (Table S9†), L′–Ga≡N–L′ (Table S10†), L′–In≡N–L′ (Table S11†), and L′–Tl≡N–L′ (Table S12†). The NRT values in Table 3 show that the bond order for the B≡N bond is 2.18 (L′ = SiMe(Si*t*Bu$_3$)$_2$), 2.17 (L′ = Si*i*PrDis$_2$), 2.24 (L′ = Tbt), and 2.22 (L′ = Ar*). This NRT data is similar to the WBI values (2.19, 2.16, 2.08, and 2.14, respectively) in Table 3. The NBO and NRT data in Table 3 also shows that the triply bonded L′–B≡N–L′ molecules for this study all have an analogous electronic structure. As seen in Table 3, (SiMe(Si*t*Bu$_3$)$_2$)–B≡N–(SiMe(Si*t*Bu$_3$)$_2$) is predicted to have one σ bond and two π ($\pi_{\perp}$ and $\pi_{\parallel}$) bonds, which are occupied by two electrons: that is, 1.99 (σ), 1.96 ($\pi_{\perp}$) and 1.96 ($\pi_{\parallel}$). The M06-2X results also show that the σ bond is heavily polarized towards nitrogen (78%) and that there are two non-degenerate π bonds that are also heavily polarized towards nitrogen ($\pi_{\perp}$, 80% and $\pi_{\parallel}$, 80%). This is consistent with the fact that nitrogen (3.066) is more electronegative than boron (2.051).[79] The two non-degenerate π bonding orbitals ($\pi_{\perp}$ and $\pi_{\parallel}$) are schematically given in ESI.†

Table 2 The bond lengths (Å), bond angles (°), singlet–triplet energy splitting ($\Delta E'_{\mathrm{B}}$ and $\Delta E'_{\mathrm{N}}$), natural charge densities (Q'_{B} and Q'_{N}), binding energies (BE), the Wiberg bond index (WBI), HOMO–LUMO energy gaps, and some reaction enthalpies for L′–B≡N–L′ at the M06-2X/Def2-TZVP level of theory

L′	SiMe(Si*t*Bu$_3$)$_2$	Si*i*PrDis$_2$	Tbt	Ar*
B≡N (Å)	1.257	1.242	1.273	1.267
∠L′–B–N (°)	175.2	165.2	171.9	171.2
∠B–N–L′ (°)	163.1	166.6	157.7	166.2
∠L′–B–N–L′ (°)	180.0	180.0	178.7	179.5
$Q'_{\mathrm{B}}{}^{a}$	0.2413	0.0818	−0.2133	−0.1600
$Q'_{\mathrm{N}}{}^{b}$	−0.3076	−0.4369	−0.1566	−0.1471
$\Delta E'_{\mathrm{ST}}$ for L′–B^c (kcal mol^{-1})	13.59	11.24	21.47	20.75
ΔE_{ST} for L′–N^d (kcal mol^{-1})	−22.30	−25.05	−25.52	−28.63
HOMO–LUMO (kcal mol^{-1})	103.3	114.2	66.97	68.28
BE^e (kcal mol^{-1})	380.0	383.8	375.9	426.3
$\Delta H_1{}^f$ (kcal mol^{-1})	98.78	80.03	91.69	89.84
$\Delta H_2{}^f$ (kcal mol^{-1})	94.05	71.21	92.96	75.25
WBI^g	2.188	2.161	2.078	2.135

[a] The natural charge density on boron. [b] The natural charge density on nitrogen. [c] $\Delta E'_{\mathrm{ST}}$ (kcal mol^{-1}) = E(triplet state for L′–B) − E(singlet state for L′–B). [d] $\Delta E'_{\mathrm{ST}}$ (kcal mol^{-1}) = E(triplet state for L′–N) − E(singlet state for L′–N). [e] BE (kcal mol^{-1}) = E(triplet state for L′–B) + E(triplet state for L′–N) − E(singlet for L′–B≡N–L′). [f] See Scheme 2. [g] The Wiberg bond index (WBI) for the B≡N bond: see ref. 71 and 72.

Table 3 The natural bond orbital (NBO) and natural resonance theory (NRT) analysis for L′–B≡N–R′ molecules that feature bulky ligands (L′ = SiMe(Si*t*Bu$_3$)$_2$, Tbt, Si*i*PrDis$_2$, and Ar*) at the M06-2X/Def2-TZVP level of theory[a,b]

		NBO analysis			NRT analysis	
L′–B≡N–R′	WBI	Occupancy	Hybridization	Polarization	Total/covalent/ionic	Resonance weight
L′ = SiMe(Si*t*Bu$_3$)$_2$	2.19	σ: 1.99	σ: 0.4743 B (sp$^{1.43}$) + 0.8803 N (sp$^{0.80}$)	22.50% (B) 77.50% (N)	2.18/0.88/1.30	B–N: 6.14% B=N: 69.80% B≡N: 24.06%
		$\pi_\perp$: 1.96	$\pi_\perp$: 0.4506 B (sp$^{99.99}$) + 0.8927 N (sp$^{99.99}$)	20.30% (B) 79.70% (N)		
		$\pi_\parallel$: 1.96	$\pi_\parallel$: 0.4483 B (sp$^{99.99}$) + 0.8939 N (sp$^{1.00}$)	20.10% (B) 79.90% (N)		
L′ = Si*i*PrDis$_2$	2.16	σ: 1.99	σ: 0.4747 B (sp$^{1.44}$) + 0.8801 N (sp$^{0.83}$)	22.54% (B) 77.46% (N)	2.17/0.91/1.26	B–N: 72.26% B=N: 27.74% B≡N: 0.00%
		$\pi_\perp$: 1.96	$\pi_\perp$: 0.4530 B (sp$^{99.99}$) + 0.8915 N (sp$^{99.99}$)	20.52% (B) 79.48% (N)		
		$\pi_\parallel$: 1.96	$\pi_\parallel$: 0.4430 B (sp$^{21.83}$) + 0.8965 N (sp$^{79.29}$)	19.63% (B) 80.37% (N)		
L′ = Tbt	2.08	σ: 1.99	σ: 0.4855 B (sp$^{1.34}$) + 0.8742 N (sp$^{0.81}$)	23.57% (B) 76.43% (N)	2.24/0.49/1.75	B–N: 81.96 B=N: 18.04 B≡N: 0.00%
		$\pi_\perp$: 1.94	$\pi_\perp$: 0.4515 B (sp$^{99.99}$) + 0.8923 N (sp^{1})	20.38% (B) 79.62% (N)		
		$\pi_\parallel$: 1.88	$\pi_\parallel$: 0.4433 B (sp$^{99.99}$) + 0.8964 N (sp$^{99.99}$)	19.65% (B) 80.35% (N)		
L′ = Ar*	2.14	σ: 1.99	σ: 0.4918 B (sp$^{1.30}$) + 0.8707 N (sp$^{0.84}$)	24.18% (B) 75.82% (N)	2.22/0.49/1.09	B–N: 42.68% B=N: 56.9% B≡N: 0.42%
		$\pi_\perp$: 1.95	σ: 0.4580 B (sp$^{99.99}$) + 0.8889 N (sp$^{99.99}$)	20.98% (B) 79.02% (N)		
		$\pi_\parallel$: 1.85	σ: 0.4433 B (sp$^{99.99}$) + 0.8964 N (sp$^{99.99}$)	19.65% (B) 80.35% (N)		

[a] The value of the Wiberg bond index (WBI) for the B≡N bond and the occupancy of the corresponding σ and π bonding NBO (see ref. 71 and 72). [b] NRT; see ref. 76–78.

4. Conclusions

This study uses DFT computational methods to determine the effect of both small and bulky substituents on the triple-bonded L–E$_{13}$≡N–L (E$_{13}$ = B, Al, Ga, In, and Tl) compounds, in order to determine how to successfully design and synthesize a molecule featuring an E$_{13}$≡N triple bond. This study represents the first theoretical investigation of the stability of the triply bonded L–E$_{13}$≡N–L molecules. Four important conclusions are drawn, based on the results of this theoretical study:

(1) Previous theoretical conclusions[52–64] showed that only sterically bulky ligands, and not small groups, thermodynamically stabilize the triple bond of the L–E$_{13}$≡E$_{15}$–L (E$_{13}$ = B, Al, Ga, In and Tl; E$_{15}$ = P, As, Sb and Bi) molecules. However,[52–64] this theoretical study finds that both small (but electropositive) ligands and bulky substituents stabilize the triply bonded L–E$_{13}$≡N–L compounds.

(2) The theoretical analysis shows that the bonding nature of a triply bonded L–E$_{13}$≡N–L molecule that features small substituents can be represented as L–E$_{13}$$\begin{smallmatrix}\leftarrow\\ \leftarrow\\ \rightarrow\end{smallmatrix}$N–L.

(3) The bonding character of the central triple bond in an L′–E$_{13}$≡N–L′ compound that features bulkier substituents can be regarded as L′–E$_{13}$$\begin{smallmatrix}\leftarrow\\ =\end{smallmatrix}$N–L′.

(4) Since two central heteroatoms (E$_{13}$ and N) are involved in the triply bonded L–E$_{13}$≡N–L (and L′–E$_{13}$≡N–L′) species, they belong to different rows of the periodic table so they have different quantum numbers. Therefore, E$_{13}$ and N have different electronegativity values and different atomic sizes. Due to the poor overlap populations between E$_{13}$ and N in both triply bonded L–E$_{13}$≡N–L and L′–E$_{13}$≡N–L′ molecules, it is expected that the bond order of the E$_{13}$≡N triple bond must be small, so their E$_{13}$≡N triple bonds must be weak.

The results of this theoretical study should allow the production and synthesis of stable triply bonded L–E$_{13}$≡N–L and L′–E$_{13}$≡N–L′ molecules.

Conflicts of interest

There are no conflicts to declare.

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