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PAPER

NXAl$_3^+$ (X = N, P, As): penta-atomic planar tetracoordinate nitrogen with N–X multiple bonding†

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Planar tetracoordinate nitrogen (ptN) has been successfully extended as a new branch of planar chemistry. As the simplest type of ptN, penta-atomic species (pptN, *e.g.*, NAl$_4^-$) are known to have a "delocalized" molecular environment with a single bond between the central N and the ligand. In this paper, through an extensive isomeric search of a series of group V-based systems NXAl$_3^+$ (X = N, P and As) in both singlet and triplet electronic states at the B3LYP/6-311+G(d) level, we report a class of novel pptN with unique chemical bonding, *i.e.*, the central nitrogen and the connected ligand X (X = N, P and As) effectively form a highly "localized" N–X multiple bond, as confirmed by the aug-cc-pVTZ-B3LYP and MP2 calculations. The high-level CCSD(T)/aug-cc-pVTZ energetic calculations show that the three pptN species each have appreciable kinetic stability against structural transformation and fragmentation, which is confirmed by the Born–Oppenheimer molecular dynamics calculations. Possible formation pathways of the three pptNs are discussed. In particular, the pptN isomer with X = P, *i.e.*, NPAl$_3^+$, is the global minimum, making the pptN-based NPAl$_3^+$ the most accessible *via* mass spectroscopic characterization. The present work demonstrates that the frequently used concept "localization *vs.* delocalization" in organic chemistry can also be transplanted to exotic planar chemistries like pptN.

1. Introduction

Clusters containing group III–V elements have been the focus of a number of experimental and theoretical studies due to their distinctive properties, including high-temperature high-power electronic devices and semiconductor materials.[1] Recently, the investigations relevant to the group III–V elements have been extended to the fascinating area of planar chemistry. Ever since the pioneering proposal of the planar tetracoordinate carbon (ptC) concept in the 1970s,[2] numerous theoretical and experimental investigations have identified various kinds of planar tetra-/hyper-coordinate carbon, pt/hC (where "hyper" represents coordination numbers of five or more).[3,4] Planar coordinate chemistry has even been successfully transplanted to nitrogen. The penta-atomic NSiAl$_3$ and NAl$_4^-$ with ptN were first computationally predicted on the basis of molecular orbital analysis in 1991.[5] Existence of both the neutral and anionic pptN NAl$_4$/NAl$_4^-$ was realized in 1999 by combined photoelectron spectroscopy

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and computational studies.[6] Since then, NM$_x$/NM$_x^-$ (M = (BH), Al, Ga, In; x = 4, 5) with a planar tetra-coordinate nitrogen structure has been the focus of a few experimental and theoretical studies.[7] Notably, the magic cluster NAl$_4^-$ has been taken as a building block for assembly in sandwich-like forms.[8] In addition, a few molecules with planar tetra-, penta- or hexa-coordinate nitrogen, *i.e.*, Cu$_4$H$_4$N, Ni$_4$H$_4$N, Cu$_5$H$_5$N and [(η^6-NB$_6$)$_2$M]^q [(M,q) = (Mn,1−), (Fe,0), (Co,1+), (Ni,2+)] have been successfully designed in theory.[9]

Understanding the structures and chemical bonding of clusters is not only vital in exploring the potential of applications in cluster-assembled nanomaterials or catalysis, but also it is crucial to future progress in designing structurally and electronically novel and stable clusters. For the simplest pptX (X representing carbon or non-carbons) systems, a general rule named "18 valence electron rule" has been proposed,[5,10] in which the stabilization of the pptX structure is realized through the "delocalization" of both σ and π orbitals. Such a "delocalization" electronic strategy would usually lead to a "*balanced*" bonding environment (with aesthetically beautiful structures) which is formed by choosing suitable ligand atoms (similar atomic radius and similar electronegativity). As a result, the planar center X generally forms (equally) identical single bonds with the connected ligands.[11]

Nitrogen is the neighbor of carbon on the periodic table. Yet, contrasting to the theoretically/experimentally characterized

examples of pt/hC,[3,4] species containing pt/hN are much rarer. One possible reason is that the highly electronegative nitrogen generally prefers to form "localized" bonding rather than "delocalized" bonding. In fact, very recent work has shown that isolation of the planar hexacoordinate nitrogen species NB_6^- would seem unlikely in either gas phase or assemblies due to its high thermodynamic and kinetic instability,[12] though the valence isoelectronic CB_6^{2-} possesses good kinetic stability.[4b] The contrasting stability between NB_6^- and CB_6^{2-} can be ascribed to the greater localization ability of nitrogen than of carbon.

The above situation has frustrated the design of new compounds with pt/hN structure due to the inherent disadvantageous tendency for nitrogen to form "delocalized" bonding structures. We are aware that in organic chemistry, (i) a number of compounds incorporating localized multiple bonding between two Group V elements have been isolated or spectroscopically characterized, (ii) π-electron distribution via "localization" or "delocalization" is the driving force to achieve favorable structures, and (iii) the preference for localization or delocalization lies in the bonding environment. Given this, is it possible to achieve another class of pptN species with a novel bonding pattern by means of the intrinsically "localized" preference of the N atom?

In the present paper, by means of the "localization" approach, we computationally designed a class of unique pptN
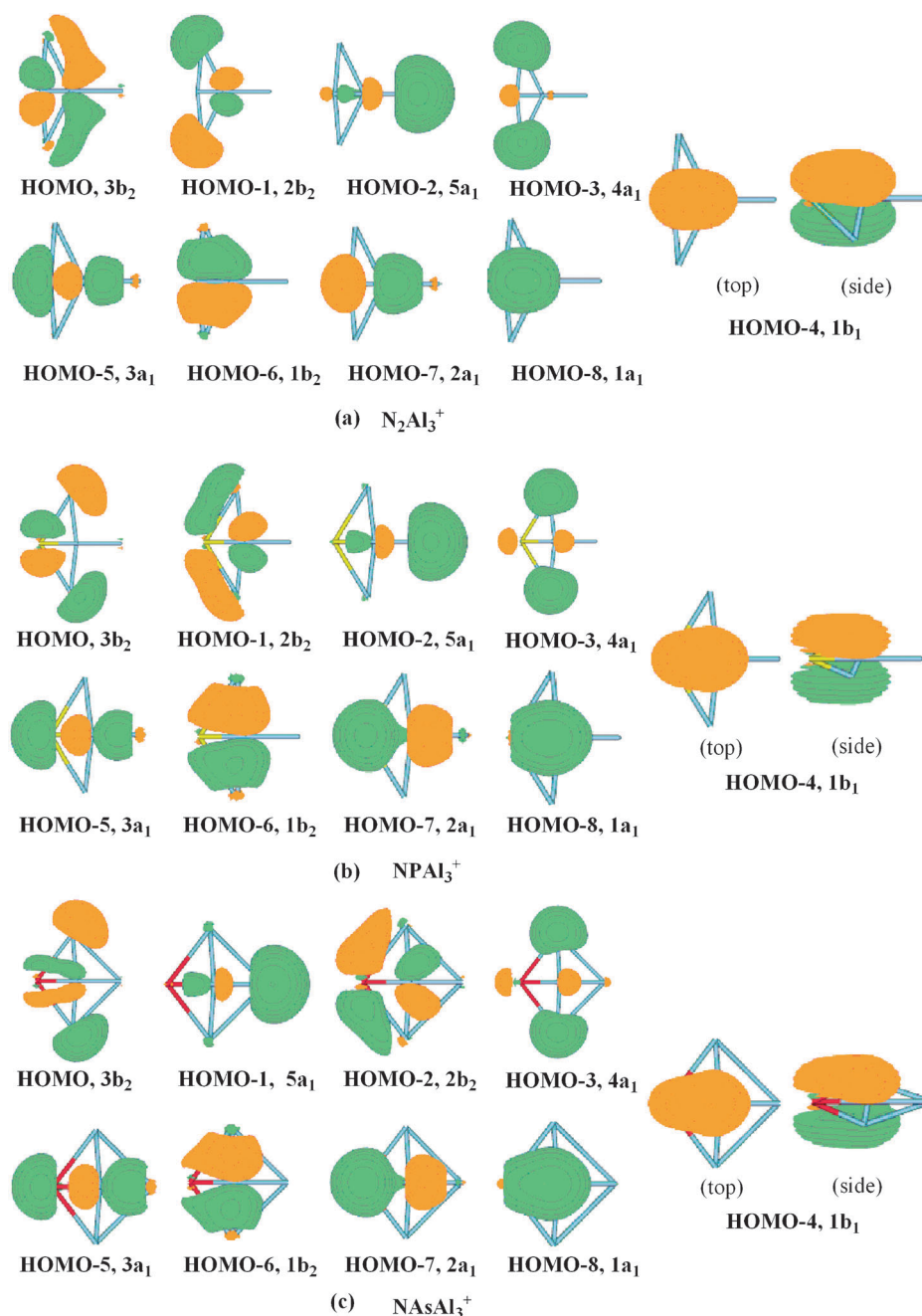

Fig. 1 Molecular orbitals of three pptNs of (a) $N_2Al_3^+$, (b) $NPAl_3^+$ and (c) $NAsAl_3^+$ at the B3LYP/aug-cc-pVTZ level.

species $NXAl_3^+$ (X = N, P and As) with highly "localized" N–X multiple bonding. The aug-cc-pVTZ-B3LYP and MP2 structural calculations and high-level CCSD(T)/aug-cc-pVTZ single-point energy calculations show that the three pptN species each have appreciable kinetic stability against structural transformation and fragmentation, which is confirmed by the Born–Oppenheimer molecular dynamics calculations. The pptN with X = P is even the corresponding global minimum, making $NPAl_3^+$ highly accessible *via* mass spectroscopic characterization.

2. Computational methods

All calculations were carried out with the GAUSSIAN03 and GAUSSIAN09 program packages.[13] The optimized geometries and harmonic frequencies of the isomers and transition states of $NXAl_3^+$ (X = N, P and As) were initially calculated using the B3LYP[14] method with the 6-311+G(d) basis set. To check the connection of each transition state, the intrinsic reaction coordinate (IRC) calculations were carried out at the B3LYP/6-31G(d) level using the B3LYP/6-31G(d) optimized geometries. In particular, for the low-lying structures, we employed the B3LYP and MP2[15] methods both with the large aug-cc-pVTZ basis set for better geometrical and frequency prediction. The

notation "**X-Tsm/n**" (X = N, P and As) stands for the interconversion transition state between the isomers **m** and **n** for $NXAl_3^+$ (X = N, P and As). High-level single-point calculations at the CCSD(T)[16]/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ levels were carried out for low-lying isomers.

3. Results and discussion

3.1 Structure and bonding of pptN

A class of penta-atomic molecules $NXAl_3^+$ (X = N, P and As) with 18 valence electrons were investigated. At the B3LYP and MP2 levels with large basis set aug-cc-pVTZ, the C_{2v} ($^1A_1$)-symmetrized penta-atomic planar tetracoordinate nitrogen (pptN) structure was located as a minimum point for each molecule. The B3LYP/aug-cc-pVTZ characteristic orbitals of the three pptN species are shown in Fig. 1. Clearly, the π-orbital $1b_1$ (HOMO-4) is mainly positioned within the N–X bond, and such localization enhances with the increase of the electronegativity of X. Such a bonding picture leads to a type of N–X multiple bonding. This is consistent with the calculated Wiberg bond index (WBI)[17] and bond distances of the three pptNs, *i.e.*, $WBI_{N–N, N–P, N–As}$ = 2.06, 1.48, 1.35 and $R_{N–N, N–P, N–As}$ = 1.230, 1.616, 1.771 Å.[18] Moreover, the two
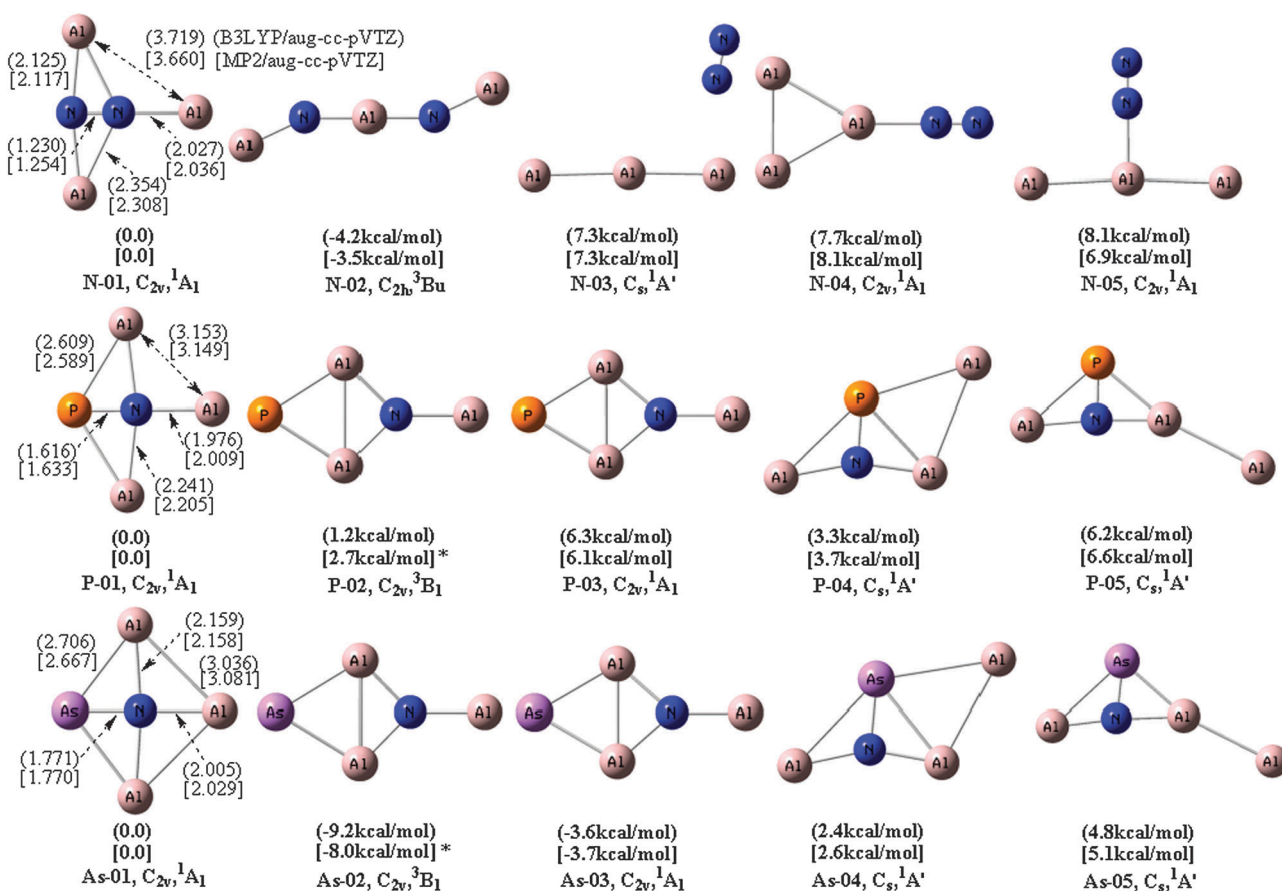

Fig. 2 The geometric structures of low-lying isomers of the three systems $NXAl_3^+$ (X = N, P and As) at the aug-cc-pVTZ-B3LYP and MP2 levels. The relative energies expressed in parentheses were obtained at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level and those in square brackets were obtained at the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level. Bond lengths are in angstroms. "*" represents the structure with C_{2v} symmetry that has an imaginary frequency at the MP2/aug-cc-pVTZ level.

identical peripheral Al–Al bonds are weakened along with the increased electronegativity of X, consistent with the Al–Al bond distances, i.e., $R_{Al–Al}$ = 3.719, 3.153 and 3.036 Å in the $N_2Al_3^+$, $NPAl_3^+$ and $NAsAl_3^+$, respectively.

The natural bond orbital (NBO) analysis of $NXAl_3^+$ (X = N, P and As) indicates the considerable charge transfer from the Al ligands to the central ptN atom, i.e., the natural population analysis (NPA) charges on the ptN are −0.88, −1.90, −2.00|e| and Al ligands are about 0.85, 0.80, 0.79|e| in the order of N to P and As, respectively. Moreover, the NPA charges of the X ligand gradually increase from negative to positive (−0.66, 0.50, 0.62|e|) along with the decreased electronegativity of X. Based on the NPA, the N–Al bonds of $NXAl_3^+$ show partial ionic character, and N–X multiple bonds show weakened covalent and increased ionic character.

3.2 Stability of ptN

3.2.1 Thermodynamic stability. We initially performed a wide structural search of the newly designed $NXAl_3^+$ (X = N, P and As) systems in both the singlet and triplet electronic states at the B3LYP/6-311+G(d) level (see SI2†). The isomers within 20 kcal mol^{-1} with reference to the corresponding ptN were further optimized at both the B3LYP/aug-cc-pVTZ and MP2/aug-cc-pVTZ levels followed by the CCSD(T)/aug-cc-pVTZ energy calculations. For simplicity, only the former low-lying isomers are given in Fig. 2 (the other isomers can be found in SI2†), among which **X-01** denotes the singlet ptN isomer, and **X-02** denotes the most stable triplet isomer. It should be noted that in **X-02**, the atoms N and X are separated either by the Al-atom (**N-02**) or by the Al–Al cross-bond (**P-02** and **As-02**). Since generally both the B3LYP and MP2-based CCSD(T) energies agree well with each other (see Fig. 2), for clarity, we only use the CCSD(T)//B3LYP energies for discussion. For $N_2Al_3^+$, the singlet ptN structure (**N-01**) is the lowest-energy singlet isomer, except that the triplet isomer **N-02** is 4.2 kcal mol^{-1} more stable. The singlet ptN structure (**P-01**) of $NPAl_3^+$ is the global minimum isomer in both the singlet and triplet states. For $NAsAl_3^+$, the singlet ptN form is 3.6 and 9.2 kcal mol^{-1} higher in energy than the lowest singlet (**As-03**) and lowest triplet (**As-02**) isomers, respectively. It is worthy of note that the stability of ptN relative to the other singlet isomers decreases in the order N, P, As, which can be ascribed to the weakened N–X multiple bonding.[19] Moreover, the low-energy isomers of $NPAl_3^+$ and $NAsAl_3^+$ are quite similar to each other in structure. Note that due to the rather strong N≡N bond, there exist three low-lying N_2-complexes, i.e., N_2···AlAlAl$^+$ **N-03** (7.3 kcal mol^{-1}), **N-05** (8.1 kcal mol^{-1}) and N_2···c-Al_3^+ **N-04** (7.7 kcal mol^{-1}). Yet, the similar structures of the NX-complex either do not exist or have high energy for $NPAl_3^+$ and $NAsAl_3^+$.

3.2.2 Kinetic stability. The kinetic stability is a fairly important factor for showing to what degree a structure can be stabilized or transformed. Thus, we explored the inter-conversion and fragmentation pathways of the designed ptN. The singlet potential energy surfaces (PESs) of the low-lying isomers of $N_2Al_3^+$, $NPAl_3^+$ and $NAsAl_3^+$ were constructed at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level, as

shown in Fig. 3a, b and c, respectively. In general, the main isomerism of the ptN **X-01** is associated with three channels, i.e., (i) ptN→ptX, (ii) Al-transfer, and (iii) bond stretch between N–X and Al–Al.

The PES of $N_2Al_3^+$ seems to be more complicated than those of $NPAl_3^+$ and $NAsAl_3^+$. With X = N, the channel (i) can be viewed as self-interconversion, and would have no influence on the kinetic stability of ptN **N-01**. The channel (ii) is an indirect Al-transfer process via the intermediate **N-07** (17.6 kcal mol^{-1}) with a total barrier of 36.9 kcal mol^{-1}. The channel (iii) needs to overcome a high barrier of 29.9 kcal mol^{-1} via **N-Ts01/08**. The main PES features of $NPAl_3^+$ and $NAsAl_3^+$ are very similar. Both involve competition between the ptN→ptX conversion (channel (i)) and direct Al-transfer (channel (ii)), i.e., 9.2 vs. 10.6 (X = P) and 9.0 vs. 9.5 kcal mol^{-1} (X = As). Also, the bond-stretch conversion (channel (iii)) needs to overcome considerable barriers, i.e., 23.7 (X = P) and 15.4 kcal mol^{-1} (X = As). By comparing the three ptN systems, we can find that in the order N, P, As: (1) the bond-stretch conversion becomes easier, (2) the Al-transfer becomes easier, and (3) the Al-transfer for X = P and As is considerably easier than for X = N (the process even becomes indirect). Point (1) can be understood by the decreased N–X double bond strength.[19] However, points (2) and (3) seem surprising since the trans-ferred Al-atom is bonded to the N-atom for all three systems. By scrutinizing the structural properties, we can obtain the answer to this. As shown in Fig. 2, the two identical peripheral Al–Al distances for X = N (3.719 Å) is much longer than those for X = P (3.153 Å) and X = As (3.036 Å), due to the much larger electronegativity of N than P and As. The abnormally long Al–Al distance results in the very difficult Al-transfer via a high-energy intermediate **N-07**. It is worth mentioning that in spite of the low energy of N_2···AlAlAl$^+$ **N-03** (7.3 kcal mol^{-1}), **N-05** (8.1 kcal mol^{-1}) and N_2···c-Al_3^+ **N-04** (7.7 kcal mol^{-1}), their formation from ptN **N-01** has a high barrier of 25.7 kcal mol^{-1}. In all, the designed three ptN species either possess the lowest energy in singlet (X = N and P) or are kinetically prohibited towards conversion to slightly lower-energy isomer (X = As). Therefore, the ptN isomers **X-01** can be viewed as having good isomeric stability.

In addition to the isomeric stability, investigation of fragmentation kinetics can provide valuable information for understanding the stability of the clusters. Table 1 lists the relative energies of various dissociation products. We can see that except for N_2 + c-$^3Al_3^+$ (9.0 kcal mol^{-1}) and N_2 + l-Al_3^+ (10.1 kcal mol^{-1}), all the other fragments are at least 30 kcal mol^{-1} higher than the ptN **X-01**, which already shows kinetic difficulty for fragmentation. As discussed above, dissociation to N_2 + c-$^3Al_3^+$ and N_2 + l-Al_3^+ is kinetically hindered. As a result, we can say that the newly designed three ptN isomers are kinetically very stable against fragmentation.

To further check the dynamic stability of the novel class of ptN species (**X-01**), we performed for each ptN the Born–Oppenheimer molecular dynamics (BOMD)[20] simulation at 373 K. The MD trajectories (see SI3†) show that each ptN keeps intact during the period of 14 ps at the B3LYP/6-31G(d) level. The MD trajectories imply that each ptN structure is
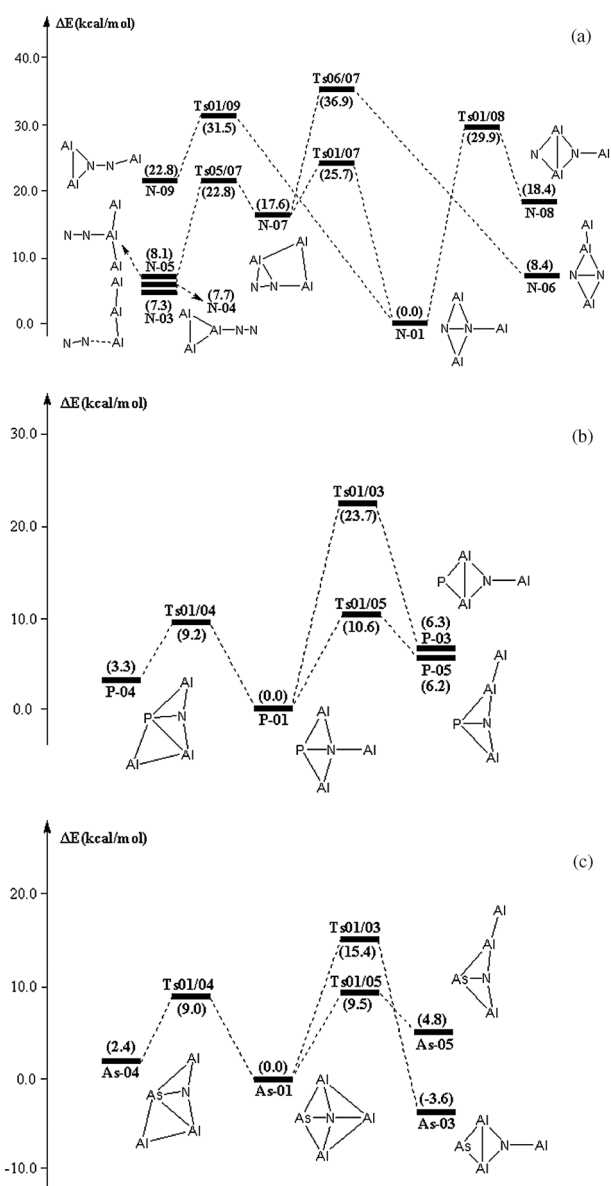
Fig. 3 Schematic potential energy surfaces of **(a)** $N_2Al_3^+$, **(b)** $NPAl_3^+$ and **(c)** $NAsAl_3^+$ obtained at the B3LYP/aug-cc-pVTZ level. The relative energies are computed at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level. "**X-Tsm/n**" stands for the interconversion transition state between the isomers **m** and **n** of $NXAl_3^+$ (X = N, P and As). For simplicity and to avoid crowding, the label "**X-**" is not shown. In (a), the connection between **N-03** and **N-05**, **N-04** and **N-05** are confirmed by a scanning strategy by fixing the bond angle.

considerably kinetically stable. There should be no nearby low-energy isomers that can be reached by **X-01** by crossing barriers. Therefore, we concluded that the newly designed pptNs could be considered as kinetically stable with regard to experimental realization.

3.3 Possible formation of pptN

From the listed fragmentation channels in Table 1, we can propose some relevant formation pathways. A general

formation pathway is to start from the fragments c-$NXAl_2$ + Al^+. The molecule N_2Al_2 (X = N) has been experimentally characterized.[21] It has a singlet ground rhombic structure with N–N cross-bonding,[22] just like the subunit of the pptN **N-01**. Thus, the direct addition of Al^+ (with one vacant orbital) to one of the N-sites via the effective donor–acceptor interaction would barrierlessly lead to the desired pptN structure. To our knowledge, $NPAl_2$ and $NAsAl_2$ have not been previously studied either experimentally or theoretically. According to our own calculation, both $NPAl_2$ and $NAsAl_2$ also have the ground symmetric C_{2v} structure with the N–X cross-bond. Therefore, interaction with Al^+ at the more negative N site should also preferentially form the pptN **P-01** and **As-01**. We should note that due to the large exothermicity from $NXAl_2$ + Al^+, i.e., 33.4 (X = N), 35.9 (X = P) and 35.9 (X = As) kcal mol^{-1}, transformation from the initially formed pptN **X-01** to other low-lying isomers is possible. Yet, since the pptN structure is the ground state on the singlet PES for X = N and P, after a long duration and a significant pressure effect, the pptN structure should be the final state. For X = As, since the singlet isomer **As-03** is 3.6 kcal mol^{-1} more stable, one needs to consider the application of sufficient pressure stabilization to obtain the pptN **As-01**.

For $N_2Al_3^+$, there exist lower-lying fragmentation channels, i.e., N_2 + c-$^3Al_3^+$ (9.0 kcal mol^{-1}) and N_2 + l-Al_3^+ (10.1 kcal mol^{-1}). The former is usually associated with the triplet PES, which could not lead to the singlet pptN. The latter can initially form the N_2-complexes **N-03** (7.3 kcal mol^{-1}), **N-04** (7.7 kcal mol^{-1}) and **N-05** (8.1 kcal mol^{-1}). Subsequently, a very high barrier of 25.7 kcal mol^{-1} is needed to reach the pptN **N-01**. So, in such a way, high temperature is necessary.

The three pptN species $N_2Al_3^+$, $NPAl_3^+$ and $NAsAl_3^+$ are mono-cationic and are very suitable for mass spectroscopic detection via the low-temperature ion–molecule reactions between singlet Al^+ (ground state) and singlet c-$NXAl_2$ (ground state). The low-lying "singlet" pptN isomers $NXAl_3^+$ (X = N, P and As) could all be generated and characterized mass spectroscopically, since the singlet–triplet intersystem crossing is usually prohibited. In the atom-aggregation processes (e.g., molecular beam experiment) followed by temperature annealing, characterization of the global minimum pptN-based $NPAl_3^+$ should be the most likely.

3.4 Implications

Over the past 30 years, planar tetra- and hyper-coordinate molecules have continued to attract great attention from experimental and theoretical chemists.[3–9,23] Designing and understanding the stability of these exotic planar molecules have greatly broadened scientists' imaginations, and most importantly, have advanced a fundamental concept in molecular architecture. Unfortunately, the planar tetra- and hyper-coordinate skeleton has to be controlled by both electronic and mechanical factors,[2a,4f,24] which could explain the rather limited number of planar coordinate examples compared to the rich chemistry in other fields. Thus, the successful design of such structures should be considered as an ongoing challenge.

5964 | *Phys. Chem. Chem. Phys.*, 2011, **13**, 5960–5966

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Table 1 The fragments of $N_2Al_3^+$, $NPAl_3^+$ and $NAsAl_3^+$. The relative energy values are in kcal mol^{-1} at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level

$N_2Al_3^+$	ΔE	$NPAl_3^+$	ΔE	$NAsAl_3^+$	ΔE
$N_2 + c\text{-}^3Al_3^+$	9.0	$c\text{-}NPAl_2 + Al^+$	35.9	$c\text{-}NAsAl_2 + Al^+$	35.9
$N_2 + l\text{-}Al_3^+$	10.1	$^4P + c\text{-}^2NAl_3^+$	56.9	$^4As + c\text{-}^2NAl_3^+$	45.9
$c\text{-}N_2Al_2 + Al^+$	33.4	$c\text{-}^2NPAl_2^+ + {}^2Al$	61.7	$c\text{-}^2NAsAl_2^+ + {}^2Al$	63.3
$c\text{-}^2N_2Al_2^+ + {}^2Al$	44.4	$l\text{-}^2NPAl + {}^2Al_2^+$	65.9	$l\text{-}^2NAsAl + {}^2Al_2^+$	71.7
$l\text{-}N_2Al^+ + {}^3Al_2$	43.1	$NP + c\text{-}^3Al_3^+$	74.6	$l\text{-}NAsAl^+ + {}^3Al_2$	87.0
$l\text{-}^2N_2Al + {}^2Al_2^+$	51.0	$NP + l\text{-}Al_3^+$	75.8	$NAs + c\text{-}^3Al_3^+$	87.6
$^4N + c\text{-}^2NAl_3^+$	74.3	$l\text{-}NPAl^+ + {}^3Al_2$	78.7	$l\text{-}^2NAl_2 + {}^3AsAl^+$	87.9
$^3NAl + l\text{-}NAl_2^+$	111.4	$l\text{-}NAl_2^+ + {}^3PAl$	100.9	$NAs + l\text{-}Al_3^+$	88.7
$^4NAl^+ + l\text{-}^2NAl_2$	128.7	$l\text{-}^2NAl_2 + {}^4PAl^+$	101.0	$l\text{-}NAl_2^+ + {}^3AsAl$	92.6
$^3N^+ + c\text{-}NAl_3$	229.4	$^4N + c\text{-}^2PAl_3^+$	119.4	$^3As^+ + c\text{-}NAl_3$	97.4
$^2N_2^+ + c\text{-}^2Al_3$	245.9	$^3P^+ + c\text{-}NAl_3$	119.8	$^4N + c\text{-}^2AsAl_3^+$	116.4
		$^3NAl + c\text{-}^3PAl_2^+$	139.0	$^3NAl + c\text{-}^3AsAl_2^+$	133.5
		$^4NAl^+ + c\text{-}^2PAl_2$	159.5	$^4NAl^+ + c\text{-}^2AsAl_2$	156.0
		$^2NP^+ + c\text{-}^2Al_3$	203.4	$^2NAs^+ + c\text{-}^2Al_3$	204.6
		$^3N^+ + c\text{-}PAl_3$	288.6	$^3N^+ + c\text{-}AsAl_3$	287.9

Compared to the ample number of pt/hCs, we are aware of fewer examples of pt/hNs, since the N-atom (with high electronegativity) prefers to form localized bonds. While previous design strategies have centered on the "delocalization" concept, the "localization" trend of N would surely be disadvantageous in stabilizing the planar-coordinate skeletons. In this work, we definitively show that by making use of the "localization" preference of N, we can design a new class of pptN molecules, i.e., $NXAl_3^+$ (X = N, P and As), within which the central N atom is connected to one ligand X by the N–X multiple bonds. To the best of our knowledge, no pptN species with embedded N–X multiple bonds have been reported so far.

4. Conclusions

In this paper, by means of the intrinsically "localized" preference of the N atom, we successfully designed a class of novel penta-atomic compounds containing planar tetra-coordinate nitrogen, i.e., $NXAl_3^+$ (X = N, P and As) on the basis of the "localization" stabilization concept. These species intrinsically bear N–X multiple bonding between the central N and the connected X atom. The three pptN species each have appreciable thermodynamic and kinetic stability against structural transformation and fragmentation, indicated by structural, molecular orbital, Wiberg bonding, potential energy surface and BOMD analysis. We suggest that, being the global minimum, the pptN of $NPAl_3^+$ is the most accessible for future mass spectroscopic characterization.

Acknowledgements

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19 We calculated the bond energy (BE) of the N–X double bonding of HNXH (X = N, P and As) at the CCSD(T)/aug-cc-pVTZ// B3LYP/aug-cc-pVTZ level by means of the following strategy: (1) $HNXH \rightarrow {}^4N + {}^4X + 2{}^2H$; $\Delta E = E_N + E_X + 2E_H - E_{HNXH}$, (2) $XH_3 \rightarrow {}^4X + 3{}^2H$; $BE_{X-H} = 1/3 (E_X + 3E_H - E_{XH_3})$, $BE_{N-X} = \Delta E - BE_{X-H} - BE_{N-H}$. The results showed that the energy of the N–X double bond was 90.9, 81.4 and 67.7 kcal mol^{-1}

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