

Realization of an Al \equiv Al Triple Bond in the Gas-Phase Na₃Al₂⁻ Cluster via Double Electronic Transmutation

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Abstract: The discovery of homodinuclear multiple bonds composed of Group 13 elements represents one of the most challenging frontiers in modern chemistry. A classical triple bond such as N \equiv N and HC \equiv CH contains one σ bond and two π bonds constructed from the *p* orbitals perpendicular to the σ bond. However, the traditional textbook triple bond between two Al atoms has remained elusive. Here we report an Al \equiv Al triple bond in the designer Na₃Al₂⁻ cluster predicted *in silico*, which was subsequently generated by pulsed arc discharge followed by mass spectrometry and photoelectron spectroscopy characterizations. Being effectively Al²⁻ due to the electron donation from Na, the Al atoms in Na₃Al₂⁻ undergo a double electronic transmutation into Group 15 elements, thus the Al²⁻ \equiv Al²⁻ kernel mimics the P \equiv P and N \equiv N molecules. We anticipate this work will stimulate more endeavors in discovering materials using Al²⁻ \equiv Al²⁻ as a building block in the gas phase and in the solid state.

Other than the well-known dinitrogen (N \equiv N), diphosphorus (P \equiv P), and acetylene (HC \equiv CH) molecules, homodinuclear triple bonds composed of main-group elements are extremely scarce,^[1,2] and the synthesis of such species imposes a great challenge to modern chemistry. The narrative of homodinuclear triple bonds composed of Group 13 elements

started with Robinson and co-workers' synthesis of the famous digallyne molecule Na₂[ArGaGaAr] (Ar = C₆H₅-2,6-(C₆H₂-2,4,6-iPr₃)₂) featuring the shortest Ga–Ga bond on record.^[3] Even though the [ArGaGaAr]²⁻ kernel is valence-isoelectronic to acetylene, its X-ray crystallography reveals a *trans*-bent structure. The nature of the Ga–Ga bond in this digallyne has attracted considerable debate afterwards.^[4,5] Cotton et al. offered an opposing opinion by density functional theory (DFT) calculations that the Ga–Ga bond had a π -type nonbonding orbital, and the short bond length was a result of the Ar–Na⁺–Ar attractions.^[6] Power and co-workers provided similar arguments that the bonding in [RGaGaR]²⁻ ions had considerable Lewis base character at the Ga centers where electron density was accumulated.^[7] In a model system [PhGaGaPh]²⁻, Frenking and co-workers pointed out that two of the three electron pairs of the Ga–Ga bond had partial lone-pair character, hence the calculated bond order had a value typical for single bonds.^[8] Grunenberg and Goldberg pointed to the mechano-chemical weakness of this bond by calculating relaxed force constants (FCs).^[9] According to their calculations of the inverted Hessian matrix, the Ga–Ga bond (0.87 aJ Å⁻²) in a “gallyne” model compound Ga₂H₂Na₂ was found to be weaker than the Ga–Ga double bond (1.20 aJ Å⁻²) in Ga₂H₄Na₂. However, according to Schaefer, Schleyer, Robinson and co-workers' calculations,^[10] the Ga \equiv Ga triple bond was composed of two dative bonds and one π bond, thus constituting a non-classical but genuine triple bond. Using a simplified model [Ga₂H₂]²⁻, Klinkhammer^[11] supported the existence of the Ga \equiv Ga triple bond, which was claimed to be a combination of a σ bond, a π bond, and a non-classical “slipped” π bond. These studies in this phenomenal “digallyne debate” have been significant contributions to Group 13 chemistry. However, due to the *trans*-bent nature, the Ga–Ga bonding situation of these compounds does not correspond to the classical triple bond that is composed of one σ bond and two π bonds constructed from the *p* orbitals perpendicular to the σ bond, such as that in the linear HC \equiv CH.

The discovery of the B \equiv B triple bond has more fruitful results, which starts from the isolation of the OC \rightarrow B \equiv B \leftarrow CO molecule in an argon matrix at 8 K by Zhou et al.,^[12] followed by a plethora of theoretical and experimental studies of the B₂ molecule stabilized by diatomic Lewis bases such as CO, CS, N₂, NHC (N-heterocyclic carbene), BO⁻.^[13–17] Braunschweig et al. synthesized the unprecedented NHC \rightarrow B \equiv B \leftarrow NHC crystal featured the first ambient-temperature isolable diborane.^[18] Köppe and Schnöckel questioned this triple bond based on electronic interactions between the B–B bond and the two B–(NHC) bonds.^[19] However, later Grunenberg's^[20a]

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and Frenking's calculations,^[20b] Braunschweig's Raman^[21a] and NMR^[21b] spectroscopic measurements as well as chemical reactions^[21c,d] supported the existence of the B≡B triple bond in NHC→B≡B←NHC.

The search for multiple Al–Al bonds has proceeded in a step-by-step manner. In 1988, Uhl^[22] synthesized the R_2AlAIR_2 ($R = CH(SiMe_3)_2$) compound containing an Al–Al single bond. In the early 1990s, it was shown that this compound could be reduced to $[R_2AlAIR_2]^-$ anions with an increased formal bond order of 1.5.^[23–26] Recently, Inoue and co-workers^[27] reported the synthesis of a dialumene compound $RR'AlAIRR'$ ($R = tBu_2MeSi$, $R' = NHC$) stabilized by N-heterocyclic carbenes, featuring a double Al=Al bond. Immediately after Inoue's work, the $LiAl_2H_4^-$ cluster^[28] produced in an ion beam was also found to exhibit an Al=Al double bond, with an $Al_2H_4^{2-}$ kernel mimicking the isoelectronic Si_2H_4 molecule. In 2006, Power^[29] synthesized and characterized a stable $Na_2[Ar'AlAlAr']$ ($Ar' = C_6H_3-2,6-(C_6H_2-2,4,6-iPr_3)_2$) compound named dialuminyne, which was similar to digallyne^[3] and featured a *trans*-bent structure, where the Al–Al triple bond was described to contain a slipped π bond.

In view of the above discussions, we aim to design a ligandless Al≡Al triple bond that is similar to N≡N and P≡P, so that it can rule out the possibilities of resonance structures, *trans*-bent geometry, and any non-classical bonding interactions such as the slipped π bond. Hence, we used the concept of double electronic transmutation (DET), which depicts the process that by acquiring two extra electrons, an element with the atomic number Z begins to have properties that were known to only belong to the element with the atomic number $Z + 2$. Based on DET, $Al^{2-} \equiv Al^{2-}$ should be similar to P≡P. Being a stricter and narrower notion of the widely used valence-isoelectronic principle, single electronic transmutation (SET) has been successfully applied for predicting structures of various compounds as reviewed elsewhere,^[30a] including those with single^[30b,c] and double^[28] Al–Al bonds. However, no compounds have been reported so far based on the DET concept.

To experimentally examine the $Al^{2-} \equiv Al^{2-}$ prototype, we designed a $Na_3Al_2^-$ cluster in the hope that each Na atom could function as an electron donor, and the fourth electron is in the form of a negative charge. Na–Al clusters of various stoichiometries were generated with a pulsed arc cluster ionization source (PACIS)^[31] in the gas phase by discharging an Al/Na mixture target with about 1500 A, 180 V, 20 μ s pulsed arc. Experimental details are provided in the Supporting Information. The resulting mass spectrum is presented in Figure 1 A, where $Na_xAl_{5-x}^-$ ($x = 0–4$), $NaAl_3O^-$ and Al_4O^- cluster anions are observed. Oxygen atoms are from the natural oxidation of sodium. $Na_3Al_2^-$ is a magic number species with a reproducibly intense mass peak among its neighboring clusters, indicating an unusually high stability. Indeed, if the Al–Al core is successfully “transmuted” into P≡P, the $Na_3Al_2^-$ cluster might well be very stable due to the closed-shell configuration and the triple $Al^{2-} \equiv Al^{2-}$ bond.

The bonding situation of $Na_3Al_2^-$ can be better interpreted by photoelectron spectroscopy, a direct means to investigate the electronic structures of the occupied molec-

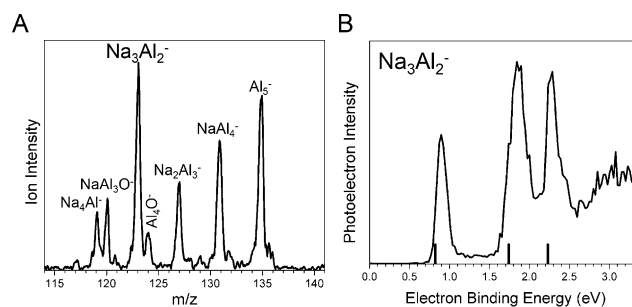


Figure 1. The mass spectrum containing $Na_3Al_2^-$ as the highest peak (A) and the anion photoelectron spectrum of $Na_3Al_2^-$ taken with 355 nm photons. The vertical bars denote the calculated VDEs from the OVGf calculations (B).

ular orbitals (MOs). In Figure 1 B, several electron binding energy (EBE) peaks at 0.89, 1.84 and 2.25 eV are assigned as the vertical detachment energies (VDE). If $Na_3Al_2^-$ is a transmuted version of P≡P, these three peaks should correspond to the photoelectrons detached from the three frontier orbitals, these being one σ bonding orbital and two π bonding orbitals, which is a direct observation of the Al≡Al triple bond.

Isolated and well-defined gas-phase systems are ideally suited for simulations employing state-of-the-art quantum theoretical methods. The unmatched high complementarity and comparability of experiment and theory in the case of gas-phase investigations bear an enormous potential for modeling challenging tasks such as global minimum (GM) search and chemical bonding analysis. To find the most thermodynamically stable structure of $Na_3Al_2^-$, we employed an unbiased search for the GM on the potential energy surface, which was expected to be the main contributor to the photoelectron spectrum. Using the Coalescence Kick (CK) program, 10000 trial structures (in singlet and triplet states) underwent geometry optimizations at PBE0/6-311 + G*, subsequently the lowest structures were recalculated at higher levels of theory (CCSD(T)/6-311 + G* and CCSD(T)/aug-cc-pVTZ//CCSD(T)/6-311 + G*), and further ranked according to their relative energies (Figure S1 and Table S1 in the Supporting Information). The GM structure of $Na_3Al_2^-$ (C_{2v} , 1A_1) exhibits a direct Al–Al contact of 2.49 Å (CCSD(T)/6-311 + G*) with three surrounding Na atoms, which define a plane passing through the center of the Al_2 core. The slight deviation from the perfect D_{3h} symmetry is stipulated by the pseudo-Jahn–Teller effect, which lowers the symmetry to C_{2v} (origin of the pseudo-Jahn–Teller distortion is presented in the Supporting Information). To verify that the GM structure of $Na_3Al_2^-$ describes the photoelectron spectrum, VDEs were computed at three levels of theory (DFT, OVGf, and CCSD(T)). As shown in Table 1, the first three VDEs unambiguously coincide with the experimental VDEs, thus confirming the computationally predicted GM structure.

The GM of the neutral Na_4Al_2 cluster (other isomers and their Cartesian coordinates are provided in Figure S2 and Table S2), which has four Na atoms positioned around the Al_2 core in the D_{4h} manner, also possesses a quite short Al–Al bond length of 2.45 Å. Being isoelectronic, both clusters are

Table 1: Experimental and calculated VDEs (eV) for the GM of Na_3Al_2^- at three levels of theory.^[a]

MO	EXPT.	OVGF	VDE	
			TD-B3LYP	CCSD(T)
HOMO (3a_1)	0.89	0.82	0.67	0.807
HOMO-1 (2a_1)	1.84	1.74	1.50	— ^[b]
HOMO-2 (1b_1)	2.25	2.23	2.54	— ^[b]

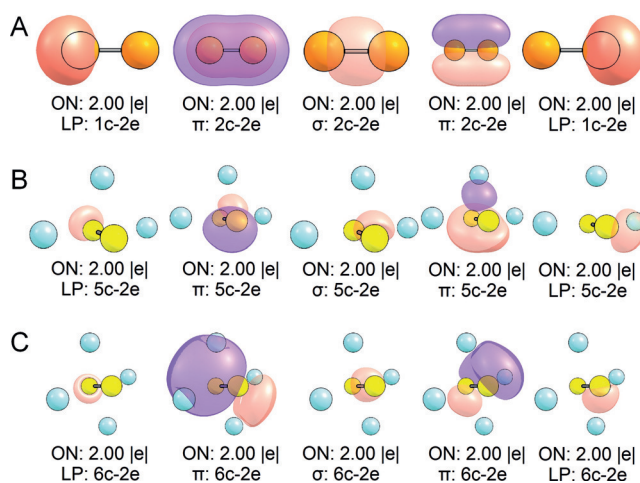
[a] Aug-cc-pVTZ basis set was employed for all three methods. [b] This VDE could not be obtained at this level of theory.

expected to form a triple $\text{Al}^2\equiv\text{Al}^{2-}$ bond, which might be the shortest for dialuminum-containing species. However, they are comparable to the $\text{Al}=\text{Al}$ double bond $\text{LiAl}_2\text{H}_4^-$ (2.46 Å),^[28] and somewhat longer than that of the di-tertbutyl(methyl)silyl-substituted dialumene (2.39 Å).^[27] We opine that it is because Al atoms carry large negative charges, which repulse each other. Other than the Al–Al distances, the Al–Al force constants $\text{FC}(\text{Al}-\text{Al})$ reflect a better measure of the bond order. According to our calculations at the PBE0/Def2-SVP level of theory employing normal coordinates within Gaussian09 program, $\text{FC}(\text{Al}-\text{Al})$ of Na_4Al_2 is 2.30 mDyne Å⁻¹, and $\text{FC}(\text{Al}-\text{Al})$ of Na_3Al_2^- is 2.02 mDyne Å⁻¹. These values are in excellent agreement with the coupled cluster values at CCSD(T)/6-311 + G*, that is, 2.41 mDyne Å⁻¹ and 2.00 mDyne Å⁻¹. Corresponding DFT values for the bulkier $\text{R}_2\text{Al}-\text{AlR}_2$ ($\text{R} = \text{CH}(\text{SiMe}_3)_2$)^[22] and $\text{RR}'\text{Al} = \text{AIRR}'$ ($\text{R} = t\text{Bu}_2\text{MeSi}$, $\text{R}' = \text{NHC}$)^[27] complexes, for which single and double Al–Al bonds have been reported, are found to be 0.68 mDyne Å⁻¹ and 1.00 mDyne Å⁻¹, respectively, thus supporting our interpretation of the $\text{Al}\equiv\text{Al}$ triple bond in Na_3Al_2^- and Na_4Al_2 . This argument is further confirmed by the relation of $\text{FC}(\text{P}-\text{P})$ of molecules with single, double and triple P–P bonds: 1.9:3.4:5.5 mDyne Å⁻¹.^[32] All these data are in accordance with the magic status of Na_3Al_2^- in the mass spectrum (Figure 1A). Contrary to the “real space” FCs, which are not invariant to the choice of the used coordinate system, relaxed FCs (compliance constants) were previously shown to provide a better measurement of the interaction strength between two atoms.^[9,33] To get more insight into the Al–Al interaction in the Na_3Al_2^- and Na_4Al_2 clusters, we calculated the relaxed $\text{FC}(\text{Al}-\text{Al})$ values using the compliance 3.0.2 program^[34] at the PBE0/Def2-SVP level of theory for Na_3Al_2^- , Na_4Al_2 , $\text{R}_2\text{Al}-\text{AlR}_2$ ($\text{R} = \text{CH}(\text{SiMe}_3)_2$)^[22] $\text{RR}'\text{Al} = \text{AIRR}'$ ($\text{R} = t\text{Bu}_2\text{MeSi}$, $\text{R}' = \text{NHC}$)^[27] systems as well as for some other prototypical model clusters where single ($\text{Al}_2\text{H}_6^{2-}$), double ($\text{Al}_2\text{H}_4\text{Na}_2$), and triple ($\text{Al}_2\text{H}_2\text{Na}_2$) Al–Al bonds are expected, in accordance with previous considerations of the corresponding Ga counterparts.^[9] The relaxed $\text{FC}(\text{Al}-\text{Al})$ values (in mDyne Å⁻¹) of Na_3Al_2^- (0.95) and Na_4Al_2 (1.08) are higher than those of the single-bonded $\text{Al}_2\text{H}_6^{2-}$ (0.61) and $\text{R}_2\text{Al}-\text{AlR}_2$ (0.80) systems, as well as of the triple-bonded $\text{Al}_2\text{H}_2\text{Na}_2$ (0.79), and are comparable to that of the double-bonded $\text{Al}_2\text{H}_4\text{Na}_2$ (1.03). Similarly to the case of model “gallyne” $\text{Ga}_2\text{H}_2\text{Na}_2$ cluster,^[9] the triple bond in $\text{Al}_2\text{H}_2\text{Na}_2$ is found to be weaker than in its double-bonded counterpart $\text{Al}_2\text{H}_4\text{Na}_2$. However, the relaxed FCs of Na_3Al_2^- and Na_4Al_2 are lower than that of the $\text{RR}'\text{Al} = \text{AIRR}'$ molecule (1.43).

Apparently, somewhat larger relaxed FC values of the species in solid state ($\text{R}_2\text{Al}-\text{AlR}_2$ ^[22] and $\text{RR}'\text{Al} = \text{AIRR}'$ ^[27]) in comparison to the corresponding model clusters ($\text{Al}_2\text{H}_6^{2-}$ and $\text{Al}_2\text{H}_4\text{Na}_2$) are associated with the presence of the bulky stabilizing ligands, which help increase the Al–Al bond strength. Hence, comparison of these numbers should be made with caution.

To further investigate the $\text{Al}\equiv\text{Al}$ triple bond, we perform the Adaptive Natural Density Partitioning (AdNDP) analysis^[35] of chemical bonding in P_2 , Na_3Al_2^- and Na_4Al_2 at the $\omega\text{B97XD}/\text{Def2-TZVP}$ level of theory (Figure 2). In both Na_3Al_2^- and Na_4Al_2 , the bonding pattern is similar to P_2 , though Na atoms contribute to the lone pair (LP) on each Al atom as well as to the σ - and π -bonds. According to AdNDP, there are two s-type lone pairs on the two Al atoms (one on each) with occupation numbers (ONs) equal to 1.64 |e| in Na_3Al_2^- and 1.63 |e| in Na_4Al_2 . The Al–Al σ -bond is found as a pure two-center two-electron (2c-2e) σ -bond with $\text{ON} = 1.85$ |e| in Na_3Al_2^- and 1.97 |e| in Na_4Al_2 . The two 2c-2e π -bonds have somewhat lower ON values: 1.30 |e|, 1.51 |e| in Na_3Al_2^- , and 1.60 |e|, 1.60 |e| in Na_4Al_2 . It is noted that the deviation of the ON values of the π -bonds from the ideal value of 2.00 |e| is in agreement with the relaxed $\text{FC}(\text{Al}-\text{Al})$ values for Na_3Al_2^- and Na_4Al_2 , which are comparable to that of the $\text{Al}_2\text{H}_4\text{Na}_2$ cluster exhibiting $\text{Al}=\text{Al}$ double bond. The analogous bonds in P_2 have ON values close to 2.00 |e| (Figure 2A). Indeed, the remaining electron density in Na_3Al_2^- and Na_4Al_2 is found on the Na atoms. Inclusion of the Na atoms into the bond search produces multicenter bonds with $\text{ON} = 2.00$ |e|, thus allowing to assess the contribution of Na atoms (Figure 2B,C).

In summary, we have applied the DET concept to design two clusters, Na_3Al_2^- and Na_4Al_2 , which are found to possess classical $\text{Al}\equiv\text{Al}$ triple bonds, although with somewhat low ON values of the direct Al–Al π bonds. Excellent agreement between the experimental and calculated VDEs for the most stable isomer of Na_3Al_2^- confirms the proposed structure. Presence of the triple bond in Na_3Al_2^- is also supported by its reproducibly intense mass peak among the neighboring

**Figure 2.** Summary of the AdNDP analysis of the P_2 (A), Na_3Al_2^- (B) and Na_4Al_2 (C) clusters.

clusters, which indicates an unusually high stability. Similarity of the canonical MOs of the $P\equiv P$ molecule with $Na_3Al_2^-$ and Na_4Al_2 , along with the AdNDP results, further confirm that Na atoms can “transmutate” Al into P, and therefore, aid in the formation of the $Al\equiv Al$ triple bonds. The $Al^{2-}\equiv Al^{2-}$ core may serve as a building block in other gas-phase clusters, and it also holds potential to be realized in periodically extended solid-state compounds. Similarly, the valence-isoelectronic triple bonded C_2^{2-} already functions as a building block of a large family of carbide compounds.^[36] Furthermore, highly charged species of the heavier homologs of Al, such as the Tl_4^{8-} and In_4^{8-} cluster anions, represent more examples of experimentally observed building blocks, which are stabilized as solid-state Zintl phases via strong Coulomb interactions with Na^+ .^[37] Hence, this work will not only serve as a general guideline for predicting novel DET clusters, but also stimulate synthesis of the unprecedented chemical solids featuring $Al^{2-}\equiv Al^{2-}$ triple bonds.

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Conflict of interest

The authors declare no conflict of interest.

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