Indium–Arsenic Molecules with an In≡As Triple Bond: A Theoretical Approach

Jia-Syun Lu,† Ming-Chung Yang,† and Ming-Der Su*,‡§

†Department of Applied Chemistry, National Chiayi University, 60004 Chiayi, Taiwan
‡Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, 80708 Kaohsiung, Taiwan

Supporting Information

ABSTRACT: The effect of substitution on the potential energy surfaces of RIn≡AsR (R = F, OH, H, CH3, and SiH3 and R′ = SiMe(SiBu3)2, SiPrDis2, and N-heterocyclic carbene (NHC)) is determined using density functional theory calculations (M06-2X/Def2-TZVP, B3PW91/Def2-TZVP, and B3LYP/LANL2DZ+dp). The computational studies demonstrate that all of the triply bonded RIn≡AsR species prefer to adopt a bent geometry, which is consistent with the valence electron model. The theoretical studies show that RIn≡AsR molecules that have smaller substituents are kinetically unstable with respect to their intramolecular rearrangements. However, triply bonded R′In≡AsR′ species that have bulkier substituents (R′ = SiMe(SiBu3)2, SiPrDis2, and NHC) occupy minima on the singlet potential energy surface, and they are both kinetically and thermodynamically stable. That is, the electronic and steric effects of bulky substituents play an important role in making molecules that feature an In≡As triple bond viable as a synthetic target. Moreover, two valence bond models are used to interpret the bonding character of the In≡As triple bond. One is model [A], which is best represented as In≡As. This interprets the bonding conditions for RIn≡AsR molecules that feature small ligands. The other is model [B], which is best represented as In≡As. This explains the bonding character of RIn≡PAsR molecules that feature large substituents.

I. INTRODUCTION

Although triply bonded compounds (RE14R) that have group 14 elements have been experimentally7–9 and theoretically10 studied extensively, similar isovalent systems (RE13R) that feature group 13 and group 15 elements have not been the subject of as many studies.8,9 This study focuses on molecules that have an indium≡arsenic triple bond, to determine whether these triply bonded molecules can be synthesized and isolated as stable compounds when they are properly substituted. These organoindium—arsenic compounds are attractive objects of study because indium arsenide (InAs) is one of the narrow bandgap group 13–15 semiconductors (Eg = 0.35 eV, 3543 nm) and has a large excitonic diameter (62 nm),10 so these species play a prominent role in semiconductor clusters and in material chemistry.11 No related studies have been found that determine the effect of substituents on molecular systems that have an indium≡arsenic triple bond; thus, this is the first report that uses theoretical methods for the synthesis of triply bonded In≡As molecules that have various substituents. The theoretical explanations for the effect of substituents (R = F, OH, H, CH3, and SiH3 and R′ = SiMe(SiBu3)2, SiPrDis2, and NHC; Scheme 1) that are described should allow the synthesis of triply bonded indium≡arsenic molecules.

II. GENERAL CONSIDERATIONS

To gain a better understanding about the attributes of the In≡As triple bond in both RIn≡AsR and R′In≡AsR′ species, it is constructive to regard RIn≡AsR as being constructed by R−In and R−As fragments (for convenience, R is used here instead of R′)

14,15 Then, comprehension of the singlet–triplet energy splitting (ΔESt) of both R−In and R−As units can help us to deliberate the bonding situations of their In≡As triple bonds. Two bonding models between R−In and R−As moieties are likely for the triply bonded RIn≡AsR molecule as schematically shown in Figure 1. According to our density functional theory (DFT) calculations (see below), it is known that R−In and R−As units exist as a singlet and a triplet, respectively, in the ground state.

On the one hand, the greater stability of the singlet state of the R−In fragment than its triplet state can result in the triplet ground state of R−As being promoted to the singlet excited state because of its smaller promotion energy (ΔE). Therefore, the bonding mode [A] can be obtained. In this bonding model,
three features must be noted as follows: (i) The most fundamental difference between indium and arsenic elements lies in their covalent radii (1.50 and 1.21 Å, respectively), which is owing to their various core electronic structures. (ii) From Figure 1, the bonding characters of the InAs triple bond are considered to be one donor—acceptor σ bond and two donor—acceptor π bonds, which can be viewed as RIn≡AsR. (iii) Because the lone pair orbital of the R–As moiety contains the valence s orbital of arsenic, it is predicted that the overlap between the p–π orbital of R–In and the lone pair orbital of R–As should be small. Accordingly, from mode [A], one may predict that the In≡As triple bond is very weak, which will be verified theoretically in the following sections.

On the other hand, the higher stability of the Triplet state of the R–As component than its singlet state can lead to the singlet ground state of R–In being excited to the triplet excited state based on its smaller advancement energy (ΔEg). As a result, the valence bond mode [B] can be acquired. As seen in Figure 1, it has to be noted that the In≡As triple bond in mode [B] is described as one conventional σ bond, one conventional π bond, and one donor—acceptor π bond, which can be represented as RIn≡AsR. Similar to the nature of mode [A], one may foresee from mode [B] that the In≡As triple bond is feeble, which will be verified on the basis of the present DFT calculations.

As a consequence, the above bonding analyses demonstrate that the singlet—triplet energy splitting (ΔEg) of both R–In and R–As components should play a decisive role in the discussion of the triple bond characteristics in the RIn≡AsR molecules.

III. Results and Discussion. III.1. Small Ligands on Substituted RIn≡AsR. For small ligands, such as R = F, OH, H, CH3, and SiH3, three different methods of DFT calculations are used (i.e., M06-2X/Def2-TZVP, B3PW91/Def2-TZVP, and B3LYP/LANL2DZ+dp) to determine the molecular properties of triply bonded RIn≡AsR species. The key geometrical parameters, the singlet—triplet energy splitting (ΔEg = Etriplet − Esinglet), the natural charge densities (Qn and Qa), the binding energies (BEs), and the highest occupied molecular orbital—lowest unoccupied molecular orbital (HOMO–LUMO) energy gaps are summarized in Table 1.

As shown in Table 1, the key parameters for the RIn≡AsR triply bonded compounds are closer to each other at the M06-2X, B3PW91, and B3LYP levels used. The computational data in Table 1 indicate that the In≡As bond distances, which fall in the range of 2.411–2.512, 2.399–2.497, and 2.432–2.546 Å, change significantly when there is a substitution. Additionally, all three DFT calculations that are shown in Table 1 demonstrate that both the R–In and the R–As units have a singlet and triplet ground state separately. Besides these, the three DFT calculations reveal that the sum of ΔEg for R–In and R–As fragments are at least +11 (M06-2X), +16 (B3PW91), and +13 (B3LYP) kcal/mol. These sums of ΔEg values strongly suggest that the bonding pattern for the triply bonded RIn≡AsR molecule possessing small ligands is best described by the bonding mode [A] that is shown in Figure 1. In particular, this bonding model analysis allows two important conclusions to be drawn. The bonding illustrations that are given in Figure 1 show that the RIn≡AsR triple bond compound favors a bent structure (mode [A]) rather than the linear structure. This prediction is confirmed by the three DFT calculations that are summarized in Table 1. Also, the bonding model [A] demonstrates that the stability of this bent geometry for the RIn≡AsR triple bond compound with small substituents is largely due to the RIn ← AsR donor—acceptor interaction. As mentioned previously, the triple bond in the RIn≡AsR compounds bearing the small groups can be depicted as follows: In≡As. Especially, the valence bond model [A] anticipates that its In≡As triple bond would be very weak. Indeed, this prediction is confirmed by the present three DFT calculations. The WB16 for the In≡As bond collected in Table 1 is estimated to be 1.54–1.77 (M06-2X), 1.55–1.80 (B3PW91), and 1.56–1.78 (B3LYP). That is, our theoretical observations strongly suggest that the RIn≡AsR molecule featuring the small substituents should possess a weak double bond rather than a the triple bond. Accordingly, these data are significant evidence that the small ligands (R) that are studied in this work cannot effectively yield triply bonded RIn≡AsR molecules.

To determine the stability of the triply bonded RIn≡AsR molecules, three theoretical methods (M06-2X/Def2-TZVP, B3PW91/Def2-TZVP, and B3LYP/LANL2DZ+dp) are used to study the potential energy surfaces for the unimolecular rearrangement reaction of the RIn≡AsR (R = F, OH, H, CH3, and SiH3) species. The reaction profiles for these are shown in Figure 2. This figure shows that there are three local minima (R,In≡As; RIn≡AsR, and In≡AsR2), which are connected by two saddle points. Figure 2 shows that regardless of the type of small substituents that are attached, the triply bonded RIn≡AsR compounds could be unstable on the potential energy surfaces and easily undergo a 1,2-migration reaction to produce the most stable isomers, which contain an In≡As double bond. This theoretical study shows that there is a slim possibility of observing RInAsR molecules that feature an In≡As triple bond in a transient intermediate or even in a matrix (in a low-temperature experiment).
III.2. Large Ligands on Substituted R′In≡AsR′. It is easy to imagine that bulky substituents (R′) should destabilize both R′In≡As and In≡AsR′, isomers because of severe steric congestions. This, in turn, makes the triply bonded R′In≡AsR′ molecules as stable as possible. The occurrence of extraordinarily bulky substituents at both ends of the R′In≡AsR′ species protects its In≡As triple bond from attack by another substitution. Three types of bulky substituents (Scheme 1) are used to determine the effect of substituents on the stability of the indium arsenic triple bond. The structures for R′In≡AsR′ that are optimized at the B3LYP/LANL2DZ+dp//RHF/3-21G* level of theory are summarized in Table 2.

The theoretical calculations that are shown in Table 2 predict that the In≡As triple bond distance (Å) in the three bulky substituted R′In≡AsR′ species is 2.446 (R′ = SiMe(SiBu3)3), 2.430 (R′ = SiPrDis2), and 2.482 (R′ = NHC). These values are close to the previously calculated bond length for In≡As in RIn≡As molecules that contain small electropositive substituents (Table 1). Additionally, the present DFT results for the |$\Delta E_{ST}$| values (kcal/mol) of R′−In and R′−As fragments are estimated to be 16−33 and 12−16, respectively. These smaller excitation energies for the bulkier R′−In unit, compared with the higher excitation energies for the smaller R−In moiety (Table 1), strongly suggest that the bonding pattern of the R′In≡AsR′ species should select mode [B], as demonstrated in Figure 1. Namely, two triplet components ([R′−In] and [R′−As]) combine together to produce the triply bonded R′In≡AsR′ molecule at the singlet ground state. In consequence, as seen in mode [B] in Figure 1, the bonding character in the triply bonded R′In≡AsR′ compound featuring the bulky substituents is regarded as In≡As, in which the donor−acceptor π bond plays a prominent role in determining its In≡As triple bond. It has to be emphasized here that there exist two factors that affect the degree of the In≡As triple bond. One is that the lone pair orbitals of both R′−In and R′−As units contain the valence s characters. The other is that the sizes of the valence p orbitals for both bulky fragments are quite different. As a result, one can easily envision that the In≡As triple bond in such R′In≡AsR′ species should be very weak, unlike the traditional C≡C triple bond in acetylene. Indeed, the present DFT evidence given in Table 2 indicate that the WBI for SiMe(SiBu3)3−In≡As−SiMe(SiBu3)3, SiPrDis2−In≡As−SiPrDis2, and R′In≡As− SiMe(SiBu3)3, SiPrDis2, respectively...

---

Table 1. Key Geometrical Parameters, Singlet−Triplet Energy Splitting ($\Delta E_{ST}$), Natural Charge Densities ($Q_n$ and $Q_s$), BEs, and HOMO−LUMO Energy Gaps for RIn≡As Using M06-2X/Def2-TZVP, B3PW91/Def2-TZVP (in Round Brackets), and B3LYP/LANL2DZ+dp (in Square Brackets) Levels of Theory

| R            | In           | F             | OH            | H             | CH3          | SiH3         |
|--------------|--------------|---------------|---------------|---------------|--------------|--------------|
| R′In≡As      | 2.511        | 2.512         | 2.412         | 2.431         | 2.411        |
|              | (2.495)      | (2.497)       | (2.399)       | (2.418)       | (2.404)      |
|              | [2.535]      | [2.546]       | [2.432]       | [2.459]       | [2.444]      |
| R′−In−As     | 179.9        | 178.8         | 179.3         | 173.6         | 170.9        |
|              | (179.9)      | (176.9)       | (179.9)       | (173.3)       | (168.4)      |
|              | [177.8]      | [175.2]       | [179.8]       | [172.5]       | [167.4]      |
| R′−In−R      | 92.32        | 95.31         | 81.43         | 99.72         | 93.85        |
|              | (93.86)      | (96.11)       | (82.67)       | (100.4)       | (99.59)      |
|              | [91.08]      | [94.22]       | [82.28]       | [100.5]       | [102.0]      |
| Q_in         | 1.288        | 1.233         | 1.012         | 1.144         | 0.8840       |
|              | (1.196)      | (1.123)       | (0.912)       | (1.037)       | (0.7881)     |
|              | [1.343]      | [1.287]       | [1.076]       | [1.121]       | [0.9682]     |
| Q_as         | 0.138        | 0.036         | -0.624        | -0.388        | -0.767       |
|              | (0.146)      | (0.047)       | (-0.571)      | (-0.335)      | (-0.703)     |
|              | [0.077]      | [-0.005]      | [-0.591]      | [-0.367]      | [-0.748]     |
| $\Delta E_{ST}$ for In (kcal mol$^{-1}$) | 83.59        | 71.87         | 44.15         | 44.59         | 32.36        |
|              | (90.61)      | (76.67)       | (49.33)       | (46.51)       | (37.68)      |
|              | [79.43]      | [71.30]       | [44.72]       | [44.82]       | [36.24]      |
| $\Delta E_{ST}$ for As (kcal mol$^{-1}$) | -31.43       | -22.45        | -33.11        | -30.61        | -9.893       |
|              | (-32.19)     | (-22.03)      | (-33.71)      | (-30.58)      | (-8.037)     |
|              | [-30.66]     | [-20.8]       | [-31.64]      | [-28.96]      | [-25.96]     |
| BE (kcal mol$^{-1}$) | 22.14        | 18.30         | 55.83         | 53.87         | 57.82        |
|              | (19.72)      | (20.13)       | (60.95)       | (50.24)       | (57.34)      |
|              | [24.06]      | [16.32]       | [57.18]       | [53.36]       | [54.39]      |
| WBI$^{f}$    | 1.536        | 1.551         | 1.773         | 1.719         | 1.726        |
|              | (1.546)      | (1.554)       | (1.798)       | (1.758)       | (1.749)      |
|              | [1.572]      | [1.562]       | [1.780]       | [1.729]       | [1.710]      |
| HOMO−LUMO (kcal mol$^{-1}$) | 145.9        | 150.7         | 155.6         | 153.8         | 166.0        |
|              | (151.5)      | (169.5)       | (154.1)       | (157.9)       | (159.7)      |
|              | [155.0]      | [150.8]       | [140.3]       | [157.2]       | [164.5]      |

"The natural charge density on the indium atom. $^a$ The natural charge density on the arsenic atom. $^b$ $\Delta E_{ST} = E$(triplet state for R−In) − E(singlet state for R−In). $^c$ $\Delta E_{ST} = E$(triplet state for R−As) − E(singlet state for R−As). $^d$ BE = E(singlet state for R−In) + E(singlet state for R−As) − E(singlet state for RIn≡AsR). $^e$ The Wiberg bond index (WBI) for the In−As bond; see ref 18."
Substituted R. Evidence that the central In and As atoms in these bulkily substituted RInAsR molecules are strongly bonded.

As previously stated, bulky groups can destabilize the 1,2-R' migrated isomers because they crowd around one end of the central indium–arsenic bond as R'In=As: and In=AsR' (Scheme 2). Therefore, it is anticipated that bulky groups (R') prevent the isomerization of R'In=AsR' species. The B3LYP/LANL2DZ+dp calculations show that R'In=AsR' compounds that contain SiMe(SiBu3)2, SiPrDis2, and NHC groups (ΔH1 and ΔH2) are, respectively, at least 69, 76, and 72 kcal/mol higher than the corresponding RIn=AsR' compounds.

Table 2. Geometrical Parameters, Singlet–Triplet Energy Splitting (ΔE_ST), Natural Charge Densities (Qa and Qb), BEs, HOMO–LUMO Energy Gaps, WBI, and Some Reaction Enthalpy Values for R'In≡AsR' at the B3LYP/LANL2DZ+dp/3-21G* Level of Theory

| R'    | SiMe(SiBu3)2 | SiPrDis2 | NHC  |
|-------|--------------|----------|------|
| In≡As | 2.469        | 2.430    | 2.482|
| ΔR'−In−As (deg) | 165.9        | 164.8    | 171.3|
| ΔIn−As−R' (deg) | 127.8        | 120.3    | 110.8|
| ΔR'−In−As−R' (deg) | 173.9        | 172.0    | 168.3|
| Qa     | 0.874        | 0.880    | 1.021|
| Qb     | −0.783       | −0.822   | −0.359|
| ΔE_ST for In (kcal mol−1) | 32.72        | 29.94    | 15.77|
| ΔE_ST for As (kcal mol−1) | −15.31       | −22.12   | −12.37|
| BE (kcal mol−1) | 41.51        | 45.22    | 35.71|
| WBF    | 2.174        | 2.271    | 2.141|
| HOMO−LUMO (kcal mol−1) | 83.27        | 86.54    | 81.16|
| ΔH1 (kcal mol−1) | 68.8         | 76.3     | 71.8 |
| ΔH2 (kcal mol−1) | 79.4         | 85.3     | 82.8 |
| ΔH2 (kcal mol−1) | 224.4        | 242.9    | 254.8|

*See also Scheme 3. The natural charge density on the central arsenic atom. The natural charge density on the central indium atom. "ΔH1 = E(triplet state for In−R') − E(singlet state for In−R'). ΔH2 = E(triplet state for As−R') − E(singlet state for As−R'). ΔBE = E(triplet state for In=As−R') − E(singlet state for In=AsR'). ΔH1 = E(Head−tail trimer) - 3E(R'In≡AsR'); see Scheme 2. AΔH2 = E(R'In≡AsR') - E(R'In≡AsR'); see Scheme 2. ΔH1 = E(R'In≡AsR') - E(R'In≡AsR'); see Scheme 2. The WBI for the In−As bond. ΔH1 = E(In=AsR'); see Scheme 3.

As previously stated, bulky groups can destabilize the 1,2-R’ migrated isomers because they crowd around one end of the central indium–arsenic bond as R’In≡As: and In≡AsR’. (Scheme 2). Therefore, it is anticipated that bulky groups (R’) prevent the isomerization of R’In≡AsR’ species. The B3LYP/LANL2DZ+dp calculations show that R’In≡AsR’ compounds that contain SiMe(SiBu3)2, SiPrDis2, and NHC groups (ΔH1 and ΔH2) are, respectively, at least 69, 76, and 72 kcal/mol higher than the corresponding RIn≡AsR’ compounds.
more stable than the corresponding 1,2-R′ shifted isomers. Accordingly, the theoretical evidence strongly suggests that these bulkier substituents can greatly protect the central In≡As triple bond.

Because it is possible that the three R′In≡AsR′ molecules undergo trimerization reactions to yield a benzene-like product (Scheme 3), DFT is used to calculate the relevant reaction enthalpies (ΔHr), and the results are shown in Table 2. This table shows that these ΔHr energies (at least 224 kcal/mol) are so large that the bulky R′In≡AsR′ compounds cannot undergo the trimerization reactions because these reactions are prevented by the crowding that occurs when there are six bulky substituents.

NBO18 and NRT20 are also used to determine the electronic structures of the R′In≡AsR′ molecules. These are calculated at the B3LYP/LANL2DZ+dp level of theory, and the results are shown in Table 3. For instance, the NBO18 analyses for the In≡As σ bonding in SiMe(SiBu3)2−In≡As−SiMe(SiBu3)2 also give NBO(In≡As) σ = 0.441 (4s5p2.80)In + 0.898−(4s4p1.13)As. This demonstrates that the primary bonding interaction between the SiMe(SiBu3)2−In and the SiMe(SiBu3)2−As units is a result of sp(In) − p(As) donation. That is, both an electron deficiency in the In element and the π bonding orbitals (a,b) of SiMe(SiBu3)2; for comparison, see also model [B] in Figure 1.

Figure 3. Natural In≡As π bonding orbitals (a,b) of SiMe(SiBu3)2−In≡As−SiMe(SiBu3)2; for comparison, see also model [B] in Figure 1.

In≡As triple bond in this compound has a shorter single bond character (5.78%) and a shorter triple bond character (39.0%), but a larger double bond character (55.2%). The covalent part of its NRT bond order (1.55) is also longer than the ionic part (0.76). The same is true for SiPrDis2−In≡As−SiPrDis2, as shown in Table 3.21 This theoretical analysis shows that R′In≡AsR′ molecules that feature bulky substituents (R′) have a weak triple bond.

It has to be mentioned here that the NHC system is totally different from the other two bulkier compounds because NHC is a well-known strong donating ligand.13 As a result, the NHC

![image](image-url)

**Table 3. Selected Results for the Natural Bond Orbital (NBO) and the Natural Resonance theory (NRT) Analyses at the B3LYP/LANL2DZ+dp Level of Theory for R′In≡AsR′ Compounds That Have Small Substituents.a,b**

| R′In≡AsR′ | WBI | occupancy | NBO analysis | polarization | NRT analysis |
|-----------|-----|-----------|--------------|--------------|-------------|
| R′ = SiMe(SiBu3)2 | 2.17 | σ = 1.87 | σ: 0.4940 In (sp1.54) + 0.8695 As (sp1.28) | 24.41% (In) 2.31/1.55/0.76 | In−As: 57.8% |
| | | σ1: 0.4413 In (sp2.80) + 0.8974 As (sp3.13) | 75.59% (As) In−As: 55.2% |
| | | σ1: 0.4513 In (sp90.99) + 0.9143 As (sp99.99) | 80.55% (As) In−As: 39.0% |
| | | | 16.41% (In) In−As: 39.0% |
| | | | 83.59% (As) In−As: 39.0% |
| | | | 23.56% (In) In−As: 60.1% |
| | | | 76.44% (As) In−As: 56.2% |
| | | | 20.59% (In) In−As: 56.2% |
| | | | 79.41% (As) In−As: 37.70% |
| | | | 15.11% (In) In−As: 37.70% |
| | | | 84.89% (As) In−As: 37.70% |
| R′ = SiPrDis2 | 2.27 | σ = 1.87 | σ: 0.4857 In (sp1.77) + 0.8742 As (sp1.28) | 2.18/1.62/0.56 | In−As: 7.72% |
| | | σ1: 0.4537 In (sp1.80) + 0.8911 As (sp1.05) | 32.60% (In) |
| | | σ1: 0.3887 In (sp99.99) + 0.9214 As (sp1.00) | 78.30% (As) |
| | | | 23.09% (In) In−As: 78.30% |
| | | | 76.91% (As) In−As: 78.30% |
| | | | 21.73% (In) In−As: 78.30% |
| | | | 78.27% (As) In−As: 78.30% |
| R′ = NHC | 2.14 | σ = 1.80 | σ: 0.5709 In (sp1.07) + 0.8210 As (sp1.06) | 2.21/1.48/0.73 | In−As: 13.98% |
| | | σ2: 0.4805 In (sp17.18) + 0.8770 As (sp14.99) | 32.60% (In) |
| | | σ2: 0.4662 In (sp99.99) + 0.8847 As (sp99.00) | 78.30% (As) |
| | | | 23.09% (In) In−As: 78.30% |
| | | | 76.91% (As) In−As: 78.30% |
| | | | 21.73% (In) In−As: 78.30% |
| | | | 78.27% (As) In−As: 78.30% |

*aThe WBI for the In−As bond and the occupancy status for the corresponding σ and π bonding NBO (see ref 18). bNRT, see ref 20.

1176

DOI: 10.1021/acsomega.7b00113
ACS Omega 2017, 2, 1172−1179
ligand (Scheme 1) would be stabilizing the In≡As: component as a strong monovalent donor. That is, in the case of R = SiMe(SiBu)₂ or SiPrDis₂, R′=In and R′=As are covalent bonds. However, in the case of R = NHC, both NHC → In and NHC → As are donating bonds. Therefore, the (NHC)In≡As(NHC) molecule can be considered to be “donor-stabilized (coordinated) In≡As:”.

IV. CONCLUSIONS

This study uses both small and bulky groups to determine the effect of substituents on the stability of triply bonded RIn≡AsR molecules. The theoretical observations show that both the electronic and steric effects of substituents play a key role in making triply bonded RIn≡AsR synthetically accessible. It should be noted that the triple bond in the RIn≡AsR species, which is attached by bulky substituents (R’), is shown to be quite weak. These theoretical findings strongly suggest that the RIn≡AsR compounds that feature bulky substituents are easily stabilized because bulky substituents not only protect the central In≡As triple bond because there is a large steric hindrance but also prevent oligomerization reactions.

V. THEORETICAL METHODS

Triply bonded RIn≡AsR molecules have smaller ligands that consist of both organic groups (i.e., R = F, OH, H, CH₃, and SiH₃) and larger groups (i.e., R’ = SiMe(SiBu)₂, SiPrDis₂, and NHC, Scheme 1) and are studied using the hybrid DFT, using the Gaussian 09 program package. All RIn≡AsR geometries for molecules with smaller ligands (R) are fully optimized at the M06-2X/Def2-TZVP, B3PW91/Def2-TZVP, and B3LYP/Def2-TZVP, and B3LYP/LANL2DZ+dp levels of theory. Frequency calculations are executed for all structures to ensure that the transition states have only one imaginary frequency and that the reactants and products have no imaginary frequencies. The relative free energies (∆G) at 298 K are corrected at the same levels of theory.

For bulky groups (R’), the limitations of both central processing unit (CPU) time and disk memory size mean that the RHF/3-21G* calculation is used to fully optimize SiMe(SiBu)₂:In≡As:SMe(SiBu)₂, SiPrDis₂:In≡As:SiPrDis₂, and NHCl≡As:NHC. The frequencies are also computed for triply bonded R′=In≡As→R′ systems using the RHF/3-21G* method to confirm whether they are minima (no imaginary frequency) or transition states (only one imaginary frequency). To produce better energetics, the stationary points are further computed at the B3LYP/LANL2DZ+dp//RHF/3-21G* level of theory. The Cartesian coordinates, the natural bond orbitals (NBOs), and the natural resonance theory (NRT) analyses that are computed in this work at the M06-2X//Def2-TZVP, B3PW91//Def2-TZVP, and B3LYP/LANL2DZ+dp levels of theory are available as Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00113.

Cartesian coordinates, NBOs, and NRT analyses computed at the M06-2X//Def2-TZVP, B3PW91//Def2-TZVP, and B3LYP/LANL2DZ+dp levels of theory (PDF)

AUTHOR INFORMATION

Corresponding Author
E-mail: midesu@mail.ncyu.edu.tw.

ORCID

Ming-Der Su: 0000-0002-5847-4271

Author Contributions

J.-S.L. and M.-C.Y. carried out all of the theoretical computations and analyzed the results. M.-D.S. supervised the research activities and contributed to the manuscript preparation. J.-S.L., M.-C.Y., and M.-D.S. regularly discussed the progress of the research, reviewed the manuscript, and gave approval for the final version.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful to the National Center for High-Performance Computing of Taiwan for providing huge computing resources to facilitate this research. They also thank the Ministry of Science and Technology of Taiwan for the financial support. The authors extend their special thanks to reviewers 1 and 2 for their helpful suggestions and comments.

REFERENCES

(1) For recent reviews, see: (a) Power, P. P. π-Bonding and the lone pair effect in multiple bonds between heavier main group elements. Chem. Rev. 1999, 99, 3463–3504. (b) Jutzi, P. Stable system with a triple bond to silicon or its homologues: Another challenge. Angew. Chem., Int. Ed. 2000, 39, 3797–3800. (c) Weidenbruch, M. Some recent advances in the chemistry of silicon and its homologues in low coordination states. J. Organomet. Chem. 2002, 646, 39–52. (d) Power, P. P. Silicon, germanium, tin and lead analogues of acetylenes. Chem. Commun. 2003, 2091. (e) Power, P. P. Synthesis and some reactivity studies of germanium, tin and lead analogues of alkynes. Appl. Organomet. Chem. 2005, 19, 488–493. (f) Lein, M.; Krapp, A.; Frenking, G. Why do the heavy-atom analogues of acetylene E2H2 (E = Si–Pb) exhibit unusual structures? J. Am. Chem. Soc. 2005, 127, 6290–6299. . (h) Sekiguchi, A.; Ichinohe, M.; Kinjo, R. The chemistry of disilyne with a genuine Si–Si triple bond: Synthesis, structure, and reactivity. Bull. Chem. Soc. Jpn. 2006, 79, 825–832. (h) Power, P. P. Bonding and reactivity of heavier group 14 element alkyne analogues. Organometallics 2007, 26, 4362–4372. and references therein. (i) Sekiguchi, A. Disilane with a silicon–silicon triple bond: A new entry to multiple bond chemistry. Pure Appl. Chem. 2008, 80, 447–457. (j) Sekiguchi, A.; Kinjo, R.; Ichinohe, M. Interaction of π-bonds of the silicon–silicon triple bond with alkali metals: An isolable anion radical upon reduction of a disilane. Synth. Met. 2009, 159, 773–775. (k) Fischer, R. C.; Power, P. P. π-Bonding and the lone pair effect in multiple bonds involving heavier main group elements: Developments in the new millennium. Chem. Rev. 2010, 110, 3877–3923. (l) Peng, Y.; Fischer, R. C.; Merrill, W. A.; Fischer, J.; Pu, L.; Ellis, B. D.; Fettinger, J. C.; Herber, R. H.; Power, P. P. Substituent effects in ditetrel alkyne analogues: Multiple vs single bonded isomers. Chem. Sci. 2010, 1, 461–468. (m) Sasamori, T.; Han, J. S.; Hironaka, K.; Takagi, N.; Nagase, S.; Tokitoh, N. Synthesis and structure of stable 1,2-dialkyldisilane. Pure Appl. Chem. 2010, 82, 603–612.

(2) For Si≡Si, see: (a) Sekiguchi, A.; Kinjo, R.; Ichinohe, M. A stable compound containing a silicon–silicon triple bond. Science 2004, 305, 1755–1757. (b) Wilberg, N.; Vaasht, S. K.; Fischer, G.; Mayer, P. Z. Disilanes. III [1] a relatively stable disilane RSi≡Si(R = SiMe(SiBu)₂). Z. Anorg. Allg. Chem. Chem. 2004, 630, 1823–1828. (c) Sasamori, T.; Hironaka, K.; Sugiyama, T.; Takagi, N.; Nagase, S.; Hosoi, Y.; Furukawa, Y.; Tokitoh, N. Synthesis and reactions of a stable 1,2-diallyl-1,2-dibromodisilene: A precursor for substituted...
disilenes and 1,2-diallylsilylene. J. Am. Chem. Soc. 2008, 130, 13856–13857.

(3) For Ge≡Ge, see: (a) Stender, M.; Phillips, A. D.; Wright, R. J.; Power, P. P. Synthesis and characterization of a digermanium analogue of an alkyne. Angew. Chem., Int. Ed. 2002, 41, 1785–1787. (b) Stender, M.; Phillips, A. D.; Power, P. P. Formation of [ArGe(CH2)4Me]- (Ar= C6H5-2,6-Trip2; Trip = C6H2-2,6,3-H5) via reaction of ArGeGeAr with 2,3-dimethyloctane: Evidence for the existence of a Germanium analogue of an alkyne. Chem. Commun. 2002, 1312–1313. (c) Paetzold, P. Iminoboranes. Angew. Chem., Int. Ed. 2007, 46, 4251–4253. (d) Lu, J.; Vasić, B.; Zschiesche, W.; Rabezzana, R.; Schwarz, H. HCSiF and HCSiCl: The first detection of molecules with formal CSiSi triple bonds. Angew. Chem., Int. Ed. 1999, 38, 331–335, and related references therein. (b) Danovich, D.; Ogliaro, F.; Karni, M.; Apeloig, Y.; Cooper, D. L.; Shaik, S. Silynes (RC≡SiR) and disilynes (RSi≡SiR): Why are less bonds worth energetically more? Angew. Chem., Int. Ed. 2001, 40, 4023–4026. (c) Gau, D.; Kato, T.; Saffon-Mercuron, N.; Cözar, A. D.; Costiolo, F. P.; Baceiredo, A. N. To a compound with a Si–C triple bond. Angew. Chem., Int. Ed. 2010, 49, 10042–10044.

(7) For W≡W, see: (a) Wu, P.-C.; Su, M.-D. A new target for synthesis of triple bonded plumbacetylene (RC≡PbR): A theoretical design. Organometallics 2010, 30, 3293–3301. (b) Wu, P.-C.; Su, M.-D. Effects of substituents on the thermodynamic and kinetic stabilities of HCGeX (X = H, CH2, F, and Cl) isomers. A theoretical study. Inorg. Chem. 2011, 50, 6814–6822. (c) Wu, P.-C.; Su, M.-D. Theoretical designs for gemacetylene (RC≡GeR): A new target for synthesis. Dalton Trans. 2011, 40, 4253–4259.

(5) For Bi≡Bi, see: (a) Paetzold, P. Iminoboranes. Adv. Inorg. Chem. 1987, 31, 123–170. (b) Paetzold, P. Reactions at the boron-nitrogen triple bond. In Boron Chemistry, Proceedings of the 6th International Meeting on Boron Chemistry; Hermanek, S., Ed.; World Scientific: Singapore, 1987; pp 446–475. (c) Paetzold, P. New perspectives in boron nitrogen chemistry. J. Inorg. Nucl. Chem. 1991, 63, 345–350. (d) Paetzold, P. Boron–Nitrogen analogues of cyclobutadiene, benzene and cyclooctatetraene: Interconversions. Phosphorus, Sulfur Silicon Relat. Elem. 1994, 93, 39–50.

(11) For Ga≡N and In≡N, see: (a) Shaik, S.; Hiberty, P. C. In Theoretical Aspects of Physical Organic Chemistry; John Wiley & Sons Inc.: USA, 1992. (b) A. In Theoretical and Physical Principles of Organic Reactivity; John Wiley & Sons Inc.: USA, 1993. (c) Shaik, S. Progress in Physical Organic Chemistry; John Wiley & Sons Inc.: USA, 1985; Vol. 15, p 197. (d) Shaik, S.; Shibuya, P. C. In A Chemist’s Guide to Valence Bond Theory; Wiley: Interscience: USA, 2008.

(15) (a) The first paper that originated the VBSCD model sees: Shaik, S. S. What happens to molecules as they react? A valence bond approach to reactivity. J. Am. Chem. Soc. 1981, 103, 3692–3701. (b) About the most updated review of the VBSCD model, one can see: Shaik, S.; Shurki, A. Valence bond diagrams and chemical reactivity.
Angew. Chem., Int. Ed. 1999, 38, 586–625. (c) Hoffmann, R.; Shaik, S.; Hilbert, P. C. A conversation on vb vs mo theory: A never-ending rivalry? Acc. Chem. Res. 2003, 36, 750–756.

(16) Wells, A. F. In Structural Inorganic Chemistry, 5th ed.; Clarendon: USA, 1986; p 128.

(17) Kutzelnigg, W. How can one recognize a triple bond between main group elements? Angew. Chem., Int. Ed. Engl. 1984, 23, 272–295.

(18) The Wiberg bond index, which is used to screen atom pairs for the possible bonding in the natural bonding orbital (NBO) search, are performed with the NBO program. For details, see: http://www.chem.wisc.edu/~nbo5. Also, see: (a) Wiberg, K. B. Application of the pople-santrey-segal CNDO method to the cyclopropylcarbinyl and cyclobutyl cation and to bicyclobutane. Tetrahedron 1968, 1083–1096. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. Intermolecular interactions from a natural bond orbital, donor–acceptor viewpoint. Chem. Rev. 1988, 88, 899–926.

(19) (a) Pyykko, P.; Desclaux, J. P. Relativity and the periodic system of elements. Acc. Chem. Res. 1979, 12, 276–281. (b) Pyykko, P. Relativistic Effects in Structural Chemistry. Chem. Rev. 1988, 88, 563–594. (c) Pyykko, P. Strong closed-shell interactions in inorganic chemistry. Chem. Rev. 1997, 97, 597–636.

(20) (a) Glendening, E. D.; Weinhold, F. Natural resonance theory: I. General formalism. J. Comput. Chem. 1998, 19, 593–609. (b) Glendening, E. D.; Weinhold, F. Natural resonance theory: II. Natural bond order and valency. J. Comput. Chem. 1998, 19, 610–627. (c) Glendening, E. D.; Badenhoop, J. K.; Weinhold, F. Natural resonance theory: III. Chemical applications. J. Comput. Chem. 1998, 19, 628–646.

(21) It has to be pointed out that due to electropositive silyl groups (SiMe(SiBu)3 and SiPrD(Si)), the lone pairs at indium and arsenic elements would exhibit p-character to large extent, making the p–π donation much stronger. As a result, their angle ∠R–In–As is less than 180° and the angle ∠In–As–R’ is about 120°.

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. Gaussian, Inc.: Wallingford CT, 2013.

(23) Zhao, Y.; Truhlar, D. G. Density functionals with broad applicability in chemistry. Acc. Chem. Res. 2008, 41, 157–167.

(24) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. Phys. Chem. Chem. Phys. 2005, 7, 3297–3305.

(25) (a) Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. Phys. Rev. A 1988, 38, 3098–3100. (b) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 1993, 98, 5648–5652.

(26) Perdew, J. P.; Wang, Y. Accurate and simple analytic representation of the electron–gas correlation energy. Phys. Rev. B: Condens. Matter Mater. Phys. 1992, 45, 13244–13249.

(27) Lee, C.; Yang, W.; Parr, R. G. Development of the Colic–Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B: Condens. Matter Mater. Phys. 1988, 37, 785–789.

(28) (a) Dunning, T. H., Jr.; Hay, P. J. In Modern Theoretical Chemistry; Schaefer, H. F., III, Ed.; Plenum: New York, 1976; pp 1–28. (b) Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. J. Chem. Phys. 1985, 82, 270–283. (c) Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. J. Chem. Phys. 1985, 82, 284–298. (d) Wadt, W. R.; Hay, P. J. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. J. Chem. Phys. 1985, 82, 299–310. (e) Check, C. E.; Faust, T. O.; Bailey, J. M.; Wright, B. J.; Gilbert, T. M.; Sunderlin, L. S. Addition of polarization and diffuse functions to the LANL2DZ basis set for p-block elements. J. Phys. Chem. A 2001, 105, 8111–8116.