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Triply-bonded indium≡phosphorus molecules: theoretical designs and characterization†

Jia-Syun Lu,[a] Ming-Chung Yang[a] and Ming-Der Su *[ab]

The effect of substitution on the potential energy surfaces of triple-bonded RIn≡PR (R = F, OH, H, CH_3, SiH_3, NHC, $SiMe(SitBu_3)_2$ and $SiiPrDis_2$) species was investigated, using the density functional theory (*i.e.*, M06-2X/Def2-TZVP, B3PW91/Def2-TZVP and B97-D3/LANL2DZ+dp). The theoretical results suggest all of the triple-bonded RIn≡PR molecules prefer to adopt a bent form with an angle (∠In–P–R) of about 90°. Present theoretical evidence suggests only the bulkier substituents, in particular for the strong donating groups (such as the NHC group), can greatly stabilize the In≡P triple bond. In addition, bonding analyses demonstrate the bonding character of such triple-bonded RIn≡PR compounds should be represented as $\mathrm{In}\overset{\leftarrow}{\equiv}\mathrm{P}$. That is to say, the In≡P triple bond contains one traditional σ bond, one traditional π bond, and one donor–acceptor π bond. As a consequence, the theoretical findings strongly suggest the In≡P triple bond in acetylene analogues (RIn≡PR) should be very weak.

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I. Introduction

Compounds with an E_{14}≡E_{14} (E_{14} = Si, Ge, Sn, and Pb) triple bond are a new area in the inorganic field.[1,2] In 1999, in the group of Schwarz, the first example of an acetylene analogue was prepared and detected.[3] In this compound, the C≡Si triple bond is kinetically stabilized by the halogen ligands (F and Cl). After this, several alkyne analogues, such as RSi≡SiR,[4] RGe≡GeR,[5] RSn≡SnR,[6] and RPb≡PbR[7] were synthesized and structurally characterized. Besides these homologous acetylene compounds that were detected experimentally, several heteronuclear systems were also predicted theoretically.[8–10] These successful examples for synthesizing the acetylene analogues give us a hint as to whether it is possible to anticipate the stability of RE_{13}≡$E_{15}R$ (E_{13} = group 13 elements and E_{15} = group 15 elements)[11,12] species based on the effects of substituents, since the RE_{13}≡$E_{15}R$ systems are isoelectronic to the RE_{14}≡$E_{14}R$ compound from the valence electron viewpoint.

If fact, research on photochemical devices based on group 13-group 15 compound semiconductor electrodes has attracted tremendous attention over the past three decades due to their potential applications in solar energy apparatuses and the simplicity of manufacturing such electronic materials.[13–26] In particular, InP (indium phosphide) based semiconductors are promising for high-speed electron, optoelectronic, and photovoltaic devices due to their superior material properties and the possibility of developing various kinds of materials with heterostructures.[27] It is not surprising nowadays that different types of InP-based semiconductor nanowire apparatus containing field effect transistors,[28] photodetectors,[29] light-emitting devices, waveguides,[30] and solar cells[31] have been investigated using various types of heterostructures.[32–35]

Although InP has already been recognized as a useful semiconductor material, no research, including both experimental and theoretical studies, concerning molecules containing the In≡P triple bond has been carried out. The aim of this work is therefore to explore the possible existence of a triple-bonded In≡P molecule given adequate substituents. It is hoped the present studies on indium≡phosphorus triple-bonded molecules can open up a new inorganic field in the near future.

II. Results and discussion

(1) Small ligands on substituted RIn≡PR

We first used quantum-mechanical methods to examine the relative stabilities of various kinds of triple-bonded RIn≡PR molecules and the corresponding double-bonded RIn=PR species utilizing the small substituted groups (R = H, F, OH, CH_3, and SiH_3). Three kinds of density functional theory (DFT) have been utilized to investigate the potential energy surfaces of the unimolecular rearrangement reactions. The three DFT are M06-2X/Def2-TZVP, B3PW91/Def2-TZVP and B3LYP/LANL2DZ+dp. As a result, the computational results for the potential energy surfaces concerning the 1,2-migration reactions of the model molecule, RInPR (R = F, OH, H, CH_3 and SiH_3), are given in Fig. 1. From Fig. 1, one may find two kinds of 1,2-shift rearrangement reactions, *i.e.*, RIn≡PR → TS1 → R_2In=P: and RIn≡PR → TS2 → :In=PR_2. All three DFT calculated results demonstrate the

[a]Department of Applied Chemistry, National Chiayi University, Chiayi 60004, Taiwan. E-mail: midesu@mail.ncyu.edu.tw

[b]Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung 80708, Taiwan

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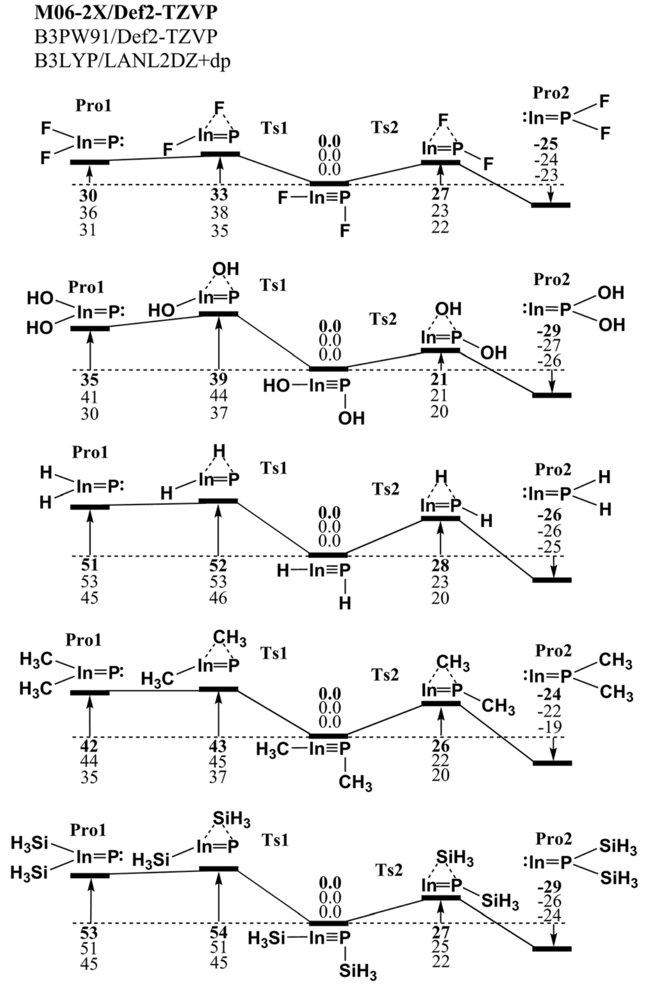


Fig. 1 The Relative Gibbs free energy surfaces for RIn≡PR (R = F, OH, H, CH_3 and SiH_3). These energies are in kcal mol^{-1} and are calculated at the M06-2X/Def2-TZVP, B3PW91/Def2-TZVP, and B3LYP/LANL2DZ+dp levels of theory. For details see the text and Table 1.

triple-bonded RIn≡PR species are neither theoretically nor kinetically stable on the intramolecular isomerization reaction surfaces. According to the present theoretical findings, it can be concluded that the experimental detections of the triple-bonded RIn≡PR molecules bearing the small substituents should be unlikely.

Despite the theoretical observations given in Fig. 1 showing the triple-bonded RIn≡PR with small groups should be very difficult to form, we still examine the physical properties of such RIn≡PR species, whose data are collected in Table 1. From Table 1, the theoretical calculations estimate the In≡P triple bond distance (Å) should be in the range of 2.312–2.422, 2.303–2.412, and 2.337–2.459 for the M06-2X/Def2-TZVP, B3PW91/Def2-TZVP (in round brackets) and B3LYP/LANL2DZ+dp (in square brackets) methods, respectively. Experimentally, however, until now the In–P single bond length is reported 2.62 Å,[36] which is slightly longer than the sum of the covalent radii (2.50 Å).[37] In addition, all the optimized geometries demonstrate they prefer to adopt the bent structures with a vertical angle (∠In–P–R ≈ 90°), as shown in Scheme 1. The reason for having such structures can be attributed to the relativistic effect discussed earlier.[38] More importantly, the three DFT calculations given in Table 1 always show the Wiberg Bond Index (WBI) of the indium–phosphorus bond is less than 2.0, meaning these RInPR species possessing the small ligands do not own the In≡P triple bond.

(2) Large ligands on substituted R′In≡PR′

Since the above section concludes the RIn≡PR molecules bearing small substituents are unlikely to be stabilized from both a thermodynamic and kinetic viewpoint, we thus turn to use the bulkier substituents (R′) to attach to indium–phosphorus to stabilize such triple-bonded R′In≡PR′ compounds for the sake of being observed experimentally. As a result, three bulkier ligands (R′ = SiMe(Si*t*Bu$_3$)$_2$,[40] SiiPrDis$_2$,[40] and NHC;[41] see Scheme 2) are utilized in this work to study the effects of substituents on the stability of triple-bonded R′In≡PR′ molecules. Since the computed systems for the R′In≡PR′ species possessing bulky ligands are so large, we thus use the B97-D3/LANL2DZ+dp[42] level of theory to investigate both their chemical and physical behaviors.

Again, we used the intramolecular 1,2-migration reaction to examine theoretically relative stabilities of the triple-bonded R′In≡PR′ compounds and its corresponding doubly bonded isomers (*i.e.*, R'_2In═P: and :In═PR'_2). See Scheme 3. The computational reaction enthalpies (*i.e.*, ΔH_1 and ΔH_2) of Scheme 3 are collected in Table 2. It is not surprising to see the energy of the triple-bonded R′In≡PR′ molecule is apparently much lower than those of both doubly bonded isomers by at least 88.0 kcal mol^{-1}, owing to steric overcrowding effects. Accordingly, the theoretical evidence strongly suggest the bulkier substituents can kinetically stabilize the triple-bonded R′In≡PR′ molecules relative to the isomeric double-bonded R'_2In═P: and :In═PR'_2 species.

According to the data from Table 2, we may use the valence-bond bonding model (Fig. 2) to interpret both bonding characters and geometrical structures of the triple-bonded R′In≡PR′ molecules featuring the bulky substituents. First, the R′In≡PR′ compound is split into two components, one is R′–In and the other is R′–P. According to the B3LYP calculations given in Table 2, it is known the R′–In fragment has the singlet ground state, while the R′–P moiety possesses the triplet ground state. As these DFT data reveal, the promotion energy from the singlet ground state to the triplet excited state for the R′–In fragment is estimated to be at least 22 kcal mol^{-1} and the promotion energy from triplet ground state to the singlet excited state for the R′–P fragment is evaluated to be at least 24 kcal mol^{-1}. One may easily conclude it would be convenient for the former to jump to the triplet excited state (compared with the data shown in Table 1). As a result, the formation of the triple-bonded R′In≡PR′ molecule at the singlet ground state can be considered the combination of two triplet fragments, *i.e.*, $[R'–In]^3$ and $[R'–P]^3$. As a consequence, from Fig. 2, the bonding scheme of the In≡P triple bond in the R′In≡PR′ species can re regarded as In⇚P, comprising one covalent σ bond, one covalent π bond and one donor–acceptor π bond. Fig. 2 shows the

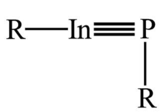
Table 1 The structural parameters, the natural charge densities (Q_{In} and Q_P), the binding energies (BE), the HOMO–LUMO energy gaps and the Wiberg Bond Index (WBI) for RIn≡PR using the M06-2X/Def2-TZVP, B3PW91/Def2-TZVP (in round brackets) and B3LYP/LANL2DZ+dp (in square brackets) levels of theory

R	F	OH	H	CH_3	SiH_3
In≡P (Å)	2.413	2.422	2.312	2.330	2.313
	(2.402)	(2.412)	(2.303)	(2.323)	(2.311)
	[2.443]	[2.459]	[2.335]	[2.359]	[2.337]
∠R–In–P (°)	179.8	178.5	179.2	176.3	176.6
	(178.0)	(177.3)	(179.7)	(178.3)	(177.2)
	[178.3]	[177.0]	[178.6]	[179.7]	[178.3]
∠In–P–R (°)	96.54	99.53	84.95	102.3	94.76
	(98.80)	(101.6)	(84.30)	(104.0)	(97.59)
	[96.13]	[99.12]	[85.10]	[104.2]	[100.4]
∠R–P–In–R (°)	180.0	179.8	177.3	178.2	179.7
	(180.0)	(179.7)	(179.9)	(179.5)	(179.2)
	[180.0]	[178.6]	[179.2]	[180.0]	[177.6]
Q_{In}[a]	1.3203	1.2598	1.0766	1.2088	0.9576
	(1.2181)	(1.1404)	(0.9760)	(1.0968)	(0.8590)
	[1.3909]	[1.3290]	[1.1458]	[1.2782]	[1.056]
Q_P[b]	0.054	−0.030	−0.7118	−0.4567	−0.8677
	(0.085)	(−0.031)	(−0.6597)	(−0.3983)	(−0.7972)
	[0.024]	[−0.008]	[−0.7054]	[−0.4721]	[−0.8762]
ΔE_{ST} for In–R[c] (kcal mol^{-1})	84.09	72.79	87.38	45.18	32.63
	(86.60)	(74.05)	(86.73)	(46.44)	(35.77)
	[81.58]	[77.81]	[83.73]	[44.43]	[38.96]
ΔE_{ST} for P–R[d] (kcal mol^{-1})	−28.91	−17.53	−30.75	−26.43	−5.804
	(−33.35)	(−21.29)	(−35.49)	(−30.26)	(−8.678)
	[−31.76]	[−20.24]	[−33.16]	[−29.21]	[−14.46]
HOMO–LUMO (kcal mol^{-1})	166.5	154.0	254.0	142.8	207.7
	(122.9)	(111.9)	(212.0)	(104.4)	(158.4)
	[187.6]	[151.4]	[317.3]	[143.5]	[169.2]
BE[e] (kcal mol^{-1})	86.99	81.76	87.38	76.85	81.65
	(86.77)	(81.41)	(86.73)	(76.05)	(81.52)
	[91.57]	[92.41]	[83.73]	[77.81]	[93.90]
WBI[f]	1.356	1.344	1.551	1.494	1.476
	(1.373)	(1.360)	(1.581)	(1.524)	(1.510)
	[1.375]	[1.352]	[1.554]	[1.507]	[1.456]

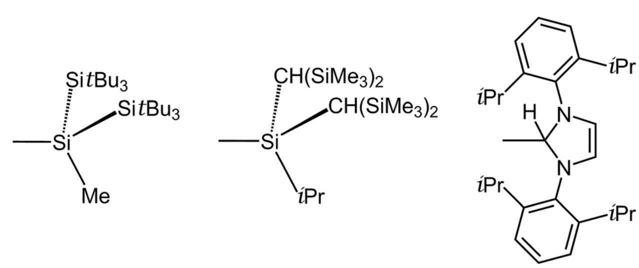
[a] The natural charge density on the central indium atom. [b] The natural charge density on the central phosphorus atom. [c] ΔE_{ST} (kcal mol^{-1}) = E(triplet state for R–In) − E(singlet state for R–In). [d] ΔE_{ST} (kcal mol^{-1}) = E(triplet state for R–P) − E(singlet state for R–P). [e] BE (kcal mol^{-1}) = E(singlet state for R–P) + E(singlet state for R–In) − E(singlet for RIn≡PR). [f] The Wiberg bond index (WBI) for the In≡P bond: see ref. 39.

lone pair orbital of the R′–P moiety includes the valence s orbital of phosphorus. This, in turn, can reduce the overlap populations between the pure p–π orbital of indium and the lone pair orbital of phosphorus. Moreover, since the quantum numbers of the valence orbitals of phosphorus are quite different from those of indium, one may imagine the overlapping populations for both covalent σ bond and covalent π bond are small as well, unlike the case of the traditional C≡C triple bond. As a consequence, one can foresee the In≡P triple bond should be weak. Indeed, as shown in Table 2, the WBI of the In≡P triple bond is estimated to be 2.16, 2.25, and 2.27 for $(SiMe(SitBu_3)_2)$–In≡P–$(SiMe(SitBu_3)_2)$, $(SiiPrDis_2)$–In≡P–$(SiiPrDis_2)$, and (NHC)–In≡P–(NHC), respectively, at the B97-D3/LANL2DZ+dp level of theory. Comparatively, the WBI of the C≡C triple bond of acetylene is calculated to be 2.99 at the same level of theory.

Similar to the cases of the triple-bonded RIn≡PR with small ligands, the DFT computations in Table 2 predict the three

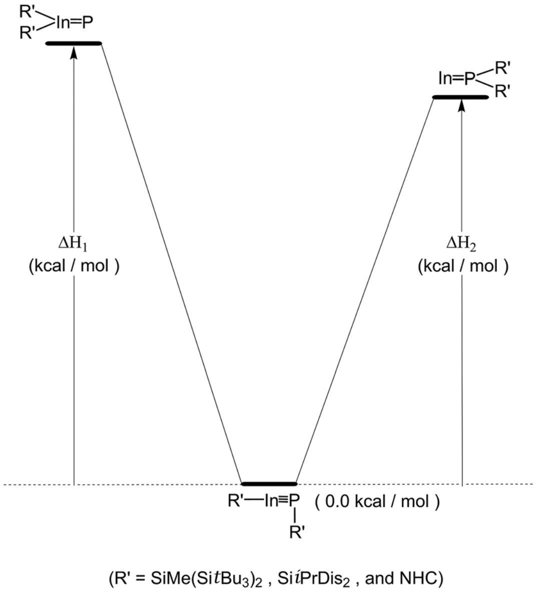


Scheme 1



$SiMe(SitBu_3)_2$ **$SiiPrDis_2$** **NHC**

Scheme 2



Scheme 3

Table 2 The bond lengths (Å), bond angels (°), singlet–triplet energy splitting (ΔE_{ST}), natural charge densities (Q_{In} and Q_P), binding energies (BE), the HOMO–LUMO energy gaps, the Wiberg bond index (WBI), and some reaction enthalpies for R′In≡PR′ at the B97-D3/LANL2DZ+dp level of theory. See also Schemes 2 and 3[a]

R′	SiMe(Si*t*Bu$_3$)$_2$	SiiPrDis$_2$	NHC
In≡P (Å)	2.362	2.337	2.315
∠R′–In–P (°)	169.6	175.0	176.7
∠In–P–R′ (°)	115.0	112.0	110.4
∠R′–In–P–R′ (°)	177.5	172.47	176.1
Q_{In}	1.1046	0.9396	0.9589
Q_P	−0.9546	−0.9363	−0.6380
ΔE_{ST} for In–R′ (kcal mol^{-1})	33.93	29.53	21.84
ΔE_{ST} for P–R′ (kcal mol^{-1})	−28.51	−27.58	−24.44
HOMO–LUMO (kcal mol^{-1})	74.96	72.41	77.66
BE (kcal mol^{-1})	86.51	84.30	106.2
ΔH_1 (kcal mol^{-1})	92.07	90.08	96.14
ΔH_2 (kcal mol^{-1})	88.35	89.18	90.43
WBI	2.263	2.251	2.174

[a] (1) The natural charge density on the central indium atom. (2) The natural charge density on the central phosphorus atom. (3) ΔE_{ST} (kcal mol^{-1}) = E(triplet state for R′–In) − E(singlet state for R′–In). (4) ΔE_{ST} (kcal mol^{-1}) = E(triplet state for R′–P) − E(singlet state for R′–P). (5) BE (kcal mol^{-1}) = E(triplet state for R′–In) + E(triplet state for R′–P) − E(singlet for R′In≡PR′). (6) See Scheme 3. (7) The Wiberg bond index (WBI) for the In≡P bond: see ref. 39.

R′In≡PR′ molecules having bulkier substituents possess the In≡P triple bond distance of about 2.3 Å. Also, the calculations anticipate their structures all choose the bent geometry with the bond angle ∠In–P–R′ being closed to 110°. That is to say, the geometrical conformations of the triple-bonded R′In≡PR′ molecules featuring the bulky ligands are quite similar to those done earlier, as schematically illustrated in Scheme 1. The reason for having such a perpendicular angle can be, again, attributed to the relativistic effects[38] as discussed earlier.

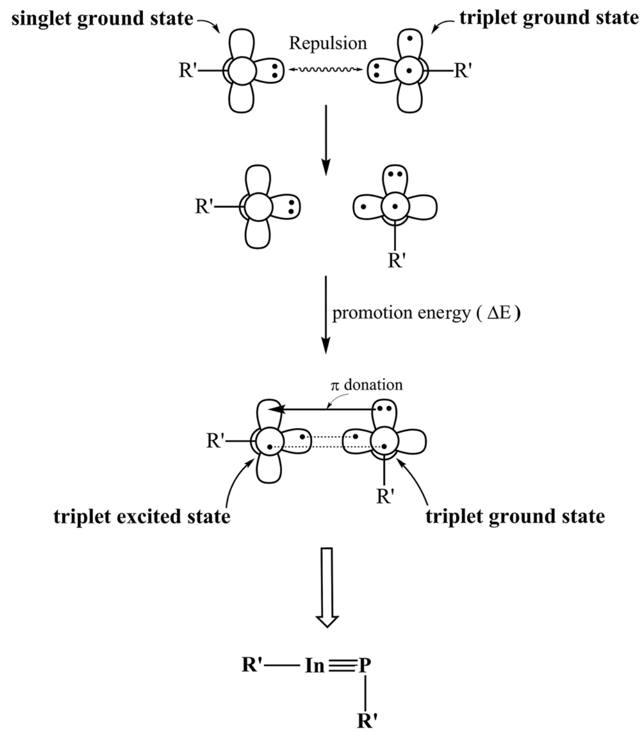


Fig. 2 The interaction model for the triply-bonded R′In≡PR′ molecule bearing the bulky substituents (R′).

To obtain further insight into the In≡P triple bond of the R′In≡PR′ species studied in this work, both the natural bond orbital (NBO)[37] and the natural resonance theory (NRT)[43] analyses were calculated, and are given in Table 3. As discussed earlier, the WBI and the NRT of three R′In≡PR′ molecules are all slightly above 2. That is, WBI = 2.17–2.26 and NRT = 2.13–2.25. All these values strongly imply the studied R′In≡PR′ molecules possessing the bulkier substituents have a weaker triple bond, which is quite different from acetylene with the traditional C≡C triple bond, whose WBI was calculated to be 2.99. Moreover, the NBO calculations summarized in Table 3 show for three R′In≡PR′ compounds both σ and π bonds are strongly polarized towards the phosphorus atom. For instance, in the case of (SiMe(Si*t*Bu$_3$)$_2$)–In≡P–(SiMe(Si*t*Bu$_3$)$_2$), its σ bond contain 69.8% (P), while its π bonds involve 85.2($\pi_\perp$)% (P) and 85.1($\pi_\parallel$)% (P). Further, its NBO analysis of the In≡P bonding interaction was computed to be as follows: π(In≡P) = 0.3845(5s5p$^{99.99}$)In + 0.9231(3s3p$^{99.99}$)P, again revealing the dominant interaction between the (SiMe(Si*t*Bu$_3$)$_2$)–In and the (SiMe(Si*t*Bu$_3$)$_2$)–P units arises from the 5p(In) ← 3p(P) donation. Its optimized wave functions representing the In≡P π bonding orbitals are shown in Fig. 3.

Besides these, it is well established NHC is a strong donating group.[41] As a result, its excellent application as a substituent for stabilizing transition-metal complexes has been unusually successful in organometallic and inorganic chemistry.[41] Likewise, one may imagine the NHC ligand utilizes its lone pair orbital to donate to the In≡P moiety. That is to say, both the NHC → In and NHC → P donating bonds can strongly stabilize

Table 3 The natural bond orbital (NBO) and the natural resonance theory (NRT) analysis for R′In≡PR′ molecules that feature ligands (R′ = SiMe(Si*t*Bu$_3$)$_2$, SiiPrDis$_2$, and NHC) at the B97-D3/LANL2DZ+dp level of theory[a,b]

		NBO analysis			NRT analysis	
R′In≡PR′	WBI	Occupancy	Hybridization	Polarization	Total/covalent/ionic	Resonance weight
R′ = SiMe(Si*t*Bu$_3$)$_2$	2.26	σ: 1.82	σ: 0.5492 In (sp$^{0.85}$) + 0.8357 P (sp$^{16.18}$)	30.16% (In) 69.84% (P)	2.24/1.66/0.58	In–P: 6.53%
		$\pi_\perp$: 1.86	$\pi_\perp$: 0.3845 In (sp$^{99.99}$) + 0.9231 P (sp$^{99.99}$)	14.78% (In) 85.22% (P)		In=P: 58.37%
		$\pi_\parallel$: 1.90	$\pi_\parallel$: 0.3856 In (sp$^{99.99}$) + 0.9227 P (sp$^{99.99}$)	14.87% (In) 85.13% (P)		In≡P: 35.10%
R′ = SiiPrDis$_2$	2.25	σ: 1.95	σ: 0.4530 In (sp$^{1.29}$) + 0.8915 P (sp$^{0.97}$)	20.52% (In) 79.48% (P)	2.25/1.84/0.41	In–P: 8.28%
		$\pi_\perp$: 1.92	$\pi_\perp$: 0.5362 In (sp$^{1.09}$) + 0.8441 P (sp$^{5.75}$)	28.75% (In) 71.25% (P)		In=P: 67.75%
		$\pi_\parallel$: 1.91	$\pi_\parallel$: 0.4330 In (sp$^{99.99}$) + 0.9014 P (sp$^{99.99}$)	18.75% (In) 81.25% (P)		In≡P: 23.97%
R′ = NHC	2.17	σ: 1.95	σ: 0.7060 In (sp$^{0.07}$) + 0.7082 P (sp$^{20.04}$)	49.85% (In) 50.15% (P)	2.13/1.69/0.44	In–P: 8.53%
		$\pi_\perp$: 1.91	$\pi_\perp$: 0.4289 In (sp$^{33.04}$) + 0.9111 P (sp$^{99.72}$)	14.14% (In) 85.86% (P)		In=P: 76.52%
		$\pi_\parallel$: 1.92	$\pi_\parallel$: 0.4117 In (sp$^{99.99}$) + 0.9113P (sp$^{99.99}$)	16.95% (In) 83.05% (P)		In≡P: 14.95%

[a] The value of the Wiberg bond index (WBI) for the In≡P bond and the occupancy of the corresponding σ and π bonding NBO (see ref. 37). [b] NRT; see ref. 43.

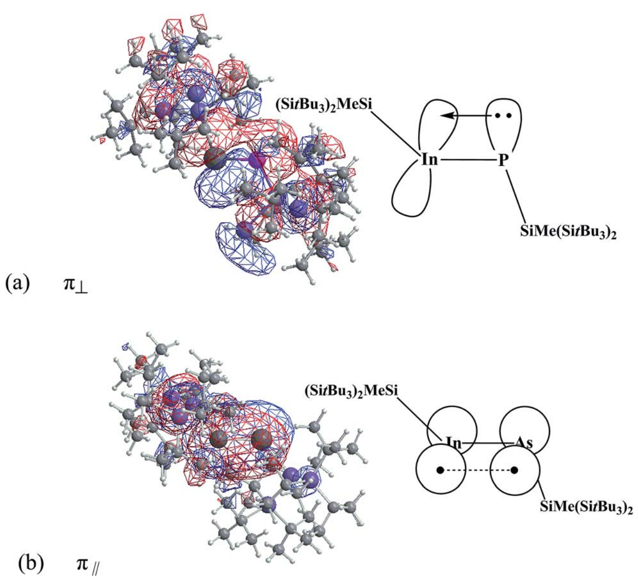


Fig. 3 The natural In≡P π bonding orbitals ((a) and (b)) for (SiMe(Si*t*Bu$_3$)$_2$)–In≡P–(SiMe(Si*t*Bu$_3$)$_2$). Also see Fig. 2.

the In≡P triple bond. Accordingly, the (NHC)–In≡P–(NHC) molecule can be considered the representation of (NHC) → In≡P ← (NHC), which should be an exciting target for future experimental synthesis and structural characterization.

III. Conclusion

In conclusion, the above theoretical evidence strongly support the concept both electronic and steric effects can greatly influence the relative stability of compounds involving an In≡P triple bond. The present theoretical investigations indicate the small organic groups, regardless of electronegativities, cannot efficiently stabilize the In≡P triple bond. Only the bulkier substituents (R′), in particular for the strong electron-donating groups (such as NHC),[41] can successfully stabilize such an In≡P triple bond. Besides these, the theoretical findings also reveal the bonding characters for the triple-bonded R′In≡PR′ species with the bulkier ligands can be represented as In$\leftleftarrows$P. Additionally, the theoretical observations demonstrate the effects come from the lone pair of phosphorus elements involving the valence s character and the different radii of the valence p orbitals in the indium and phosphorus atoms can strongly influence the chemical bonding between both elements.[44] As a consequence, the present theoretical results conclude once the triple-bonded R′In≡PR′ molecules featuring the bulkier groups are stabilized, their In≡P triple bonds should be very weak.[45]

It is hoped that the results of experimental synthesis and structural characterization will confirm these predictions.

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