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Facile [3+2] dimerization and formal dehydrogenative coupling mode of a cyanophenylphosphaallene

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This paper is dedicated to the memory of the late Professor Yoshihiko Ito

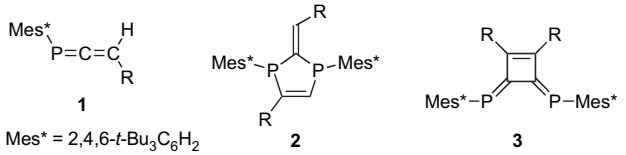
Abstract—Due to a facile head-to-tail [3+2] dimerization, even a sterically demanding group such as the Mes* (2,4,6-tri-*tert*-butylphenyl) group around the P═C═C moiety did not allow us to isolate 3-(4-cyanophenyl)-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaallene from the elimination reaction of 2-bromo-3-(4-cyanophenyl)-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaprop-1-ene with DBU (1,8-diazabicyclo-[5.4.0]undec-7-ene), and the corresponding 1,4-diphosphafulvene containing cyano groups was obtained and characterized. Theoretical studies on the [3+2] dimerization of phosphaallene characterize possible intermediates affording 1,4-diphosphafulvenes and also suggest the cyano group effect to facilitate the saturation of the P═C double bonds. On the other hand, 1,2-bis(4-cyanophenyl)-3,4-bis[(2,4,6-tri-*tert*-butylphenyl)phosphinidene]cyclobutene was obtained from 2-bromo-3-(4-cyanophenyl)-3-trimethylsiloxy-1-(2,4,6-tri-*tert*-butyl-phenyl)-1-phosphaprop-1-ene together with the 3-(4-cyanophenyl)-1-phosphaallene.

1. Introduction

A number of common N-heterocyclic compounds play important roles in science and technology. Recently, cyclic organic compounds containing phosphorus atom(s) have also attracted considerable attention in connection with the development of novel functional materials.[1,2] As an approach to the synthesis of structurally and functionally intriguing P-heterocyclic systems, we have paid considerable attention to the reactivity of the kinetically stabilized phosphaallenes **1** as a fundamental cumulative molecule containing an sp^2-type phosphorus. The chemistry of low-coordinated phosphorus compounds has intensively developed following the establishment of the kinetic stabilization technique utilizing sterically encumbered substituents to inhibit saturation of the multiple bonds of phosphorus,[3] which facilitates the use of phosphaalkenes as reagents for novel molecular transformation.

One of the intriguing P-heterocyclic systems prepared from **1** is 1,4-diphosphafulvenes **2** via a formal head-to-tail [3+2] dimerization of **1** accompanying a [1,2]-H shift (Chart 1). We recently succeeded in the formal synthesis of **2** as air-stable crystalline compounds from **1**[4–6] and revealed that one of the diphosphafulvenes **2** possesses considerable electron-donating property to afford the corresponding charge-transfer (CT) complex with 7,7,8,8-tetracyanoquinodimethane (TCNQ).[4] On the other hand, by utilizing P-heterocyclic carbene–titanocene or zirconocene complexes, Le Floch and co-workers independently reported the synthesis of 1,4-diphosphafulvenes[7] and advanced to the preparation of a cation radical derived from 1,4-diphosphafulvene.[8] These findings promise to open new research fields in organoelectronics and spintronics based on the chemistry of P-heterocyclic compounds.

Together with 1,4-diphosphafulvene derivatives, 3,4-diphosphinidenecyclobutenes (DPCBs) **3** are obtained from phosphaallene through dehydrogenative homocoupling (Chart



Mes* = 2,4,6-*t*-$Bu_3C_6H_2$

Chart 1.

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1). We previously described several DPCB formations from the corresponding phosphaallene and alkyllithium, along with the generation of hydrogen.[6b,6c] DPCBs are available as rigid P2 ligand systems with strong π-accepting characters that provide unique synthetic catalysts.[9,10]

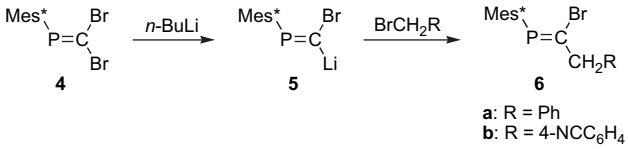
In this paper we report new findings concerning the experimental and theoretical investigations of [3+2] dimerization of **1**. In the course of studies on phosphaallenes, we found that an electron-withdrawing cyano group contributes to destabilize the phosphaallene skeleton and to facilitate [3+2] dimerization. The [3+2] dimerization of phosphaallene was assessed by DFT calculations on model compounds to depict the reaction pathways from **1** to **2**. Redox properties as well as one-electron oxidation processes of 1,4-diphosphafulvenes are also discussed. In addition, we report the preparation of a novel DPCB derivative bearing cyano groups by the use of 1-bromo-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyllithium.[6b,6c,10,11]

2. Results and discussion

2.1. Synthesis and [3+2] dimerization of phosphaallenes

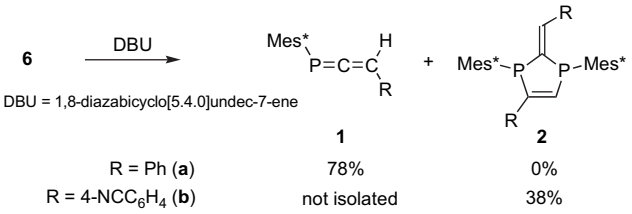
As described in our previous reports,[4–6] the reactivity of phosphaallene is strongly influenced by substituent(s) at the 3-position. In the course of our synthetical research based on the chemistry of phosphaallenes, we found that the presence of a cyano-containing substituent enhances reactivity including [2+3] dimerization to inhibit the isolation of the desired phosphaallene in spite of the presence of the bulky Mes* group.

2,2-Dibromo-1-phosphaethene **4**[12] was allowed to react with butyllithium to generate **5**, and was subsequently treated with benzyl bromide[4] or 4-cyanobenzyl bromide to afford the corresponding 2-bromo-1-phosphapropene **6** in moderate yields. The cyano group seemed to be inactive to the lithium intermediate **5** (Scheme 1).



Scheme 1.

We next examined base-induced HBr elimination of **6** with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) as shown in Scheme 2. To obtain **1a** as a single product from **6a**, DBU treatment was found suitable to give the desired **1a** in a moderate yield. On the other hand, **6b** showed considerably different reaction characteristics from **6a** in the presence of DBU. When **6b** was mixed with DBU, we observed the ^{31}P NMR signal due to **1b** [δ_P (C_6D_6) 80.2] in the reaction mixture; however, the signal due to **6b** disappeared in solution during the workup procedures, and **2b** was obtained as an isolable product as red-orange crystals. Therefore, **1b** would be considerably unstable and would dimerize in the presence of DBU at room temperature. The structure of **2b**, probably including the (R_P,R_P) and (S_P,S_P) isomers, was characterized based on spectroscopic data and was comparable to **2a**.[13]



Scheme 2.

A similar instability of phosphacumulenes in spite of the presence of the bulky Mes* group was previously reported. Märkl and co-workers found head-to-tail [2+2] P=C dimerizations of phosphabutatriene derivatives containing electron-withdrawing aryl groups at the 4-position,[14] which is comparable to the case of [3+2] dimerization of **1b** not allowing the isolation of **1b** in the presence of DBU.

2.2. DFT calculations

To illustrate the reaction pathways of the head-to-tail [3+2] dimerization of phosphaallene, we performed DFT calculations on this system starting with compound **7** as the model compound of **1**. The calculated structures for **7**, **8**, and **9** (the model compounds for **1**, **2**, and the geometrical isomer of **2**) showed comparable parameters with the experimental data of $\mathbf{1a_{Si}}$[6c] **2a**,[4] and *meso*-5-adamantylidene-1,2,3,4-tetraphenyl-1,4-diphosphafulvene,[7] respectively (Chart 2) (see Supplementary data). The energy difference between **8** and **9** is very small, and thus explains the isolation of both the *anti* and *syn* isomers of hexaphenyl-1,4-diphosphafulvene.[7]

Figure 1 depicts the calculated reaction pathways for [3+2] dimerization of **7** to **8** with three intermediary structures. As shown in Figure 2a, the metric parameters of the transition state $\mathbf{T1_{7-8}}$ of the highest energy barrier indicate that the terminal phosphorus and carbon approach each other to cause C–H bond breaking for the [1,2]-H shift and elongation of the P=C bond in molecule A. The terminal C atom of molecule A maintains the sp^2 configuration and the migrating H atom shows closer distance to the inner C atom rather than to the terminal carbon interacting with the phosphorus of molecule B. The dihedral angle of H1–P1–C1–H2 is −175.8°, suggesting that the migrating H atom interacts with the π orbital perpendicular to the P=C moiety. The HOMO and LUMO of phosphaallene[15] would play key roles in choosing one of the concerted [3+2] cyclizations to the five-membered ring skeleton. On the other hand, the structure of $\mathbf{T1_{7-8}}$ (Fig. 2a) indicates steric repulsion between

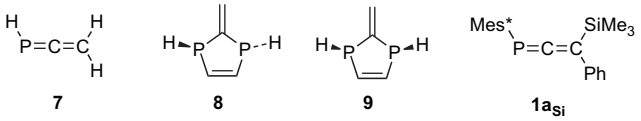


Chart 2.

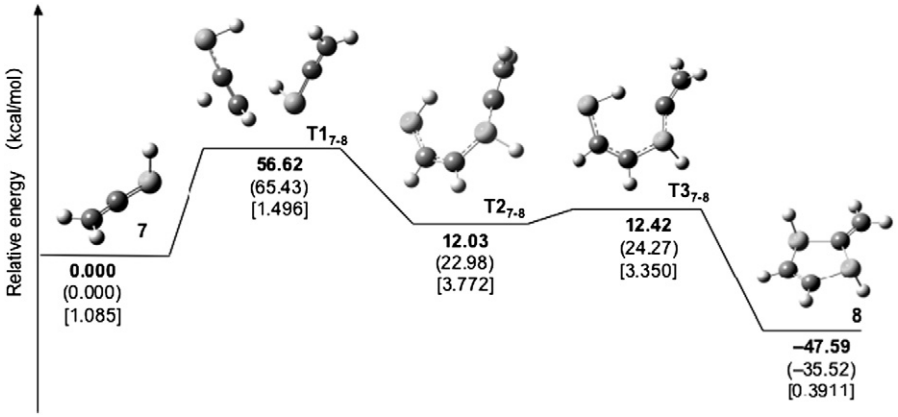


Figure 1. Computationally characterized head-to-tail [3+2] dimerization procedures of phosphaallene **7** affording **8** (B3LYP/aug-cc-pVTZ). Values in bold face correspond to relative energies (kcal/mol). Values in parentheses display Gibbs free energies (kcal/mol at 298.15 K). Values in square brackets show dipole moments (Debye).

the H atom on phosphorus of molecule A (H1) and the terminal CH_2 group of molecule B (C4, H5, H6), which prevents facile cyclization to the five-membered ring in spite of simultaneous dual P,C bond formation. Figure 2b displays the Mulliken charges of **T1$_{7-8}$** together with that of **7**. The terminal P and C atoms of molecule A are more negative and the migrating H atom shows increased positive charge, whereas molecule B shows a polarized structure [HP^{-}–C^{+}=CH_2] in comparison with **7**. Such polarized structure of phosphaallene was suggested in previously reported computations.[15] The calculation for the reaction from **7** to **8** indicates that conformational changes from intermediary **T2$_{7-8}$** to **T3$_{7-8}$** including π-electron delocalization are required. Figure 3 shows the calculated reaction pathways from **7** to **9**. In contrast to the case of the reaction from **7** to **8**, no intermediates such as **T2$_{7-8}$** were obtained for the change from **T1$_{7-9}$** to **9**. However, the parameters of **T1$_{7-9}$** are comparable with **T1$_{7-8}$** (the imaginary frequency mode of both with **T1$_{7-8}$** and with **T1$_{7-9}$** is mainly the [1,2]-H shift), indicating non-permitted overlap between the central C atoms to separate the left P=C and the right C=C moieties. Nevertheless, in the case of **T1$_{7-9}$**, the simultaneous P,C bond formation to **9** would not be prevented due to the absence of the steric repulsion discussed on the structure of **T1$_{7-8}$**. Thus, orientation of the substituents around the P=C=C moiety would control the dimerization mechanism leading to the selective formation of **8** or **9**. The high potentials of **T1$_{7-8}$** and **T1$_{7-9}$** might be reduced in the presence of bases facilitating the [1,2]-H migration. Those activation energies for the [3+2] dimerization might be overcome by the presence of a base to accelerate the polarized structure, as shown in Figure 2. Furthermore, phosphaallenes bearing an electron-withdrawing aryl substituent would easily dimerize to the corresponding 1,4-diphosphafulvene, and indeed isolation of phosphaallene **1b** in the presence of DBU was practically impossible (Scheme 2).[16]

2.3. Physicochemical properties of 1,4-diphosphafulvenes

Although novel 1,4-diphosphafulvene **2b** exhibits similar AB signals to **2a** in ^{31}P NMR, several different physicochemical properties were observed. In the UV absorption spectrum, the absorptions of **2b** show considerable red shifts compared with **2a** (256, 417 nm)[4], probably due to the reduction of the HOMO–LUMO gap. Cyclic voltammetric analyses of **2b**, on the other hand, indicate lower stability of the generating cationic species [E_p^{ox} +0.67 V, +1.30 V (sh), +1.58 V] (Fig. 4), whereas **2a** shows a reversible oxidation potential ($E_{1/2}$+0.53 V).[4] In the cathodic processes, the reduction potentials of **2b** [E_p^{red} −0.63 V (sh), −0.77 V] are comparable to **2a** [E_p^{red} −0.68 V]. Despite the reduced electron-donating property, **2b** and TCNQ formed a charge-transfer complex that was confirmed by qualitative observation of TCNQ anion radical (see Supplementary data). Effects of the cyano groups of **2b** on the 1,4-diphosphafulvene moiety are too complicated to characterize the photo- and electrochemical properties precisely, and therefore more detailed analyses are required to clarify the substituent effects.

2.4. Preparation of novel DPCB derivatives carrying cyanophenyl groups

3,4-Diphosphinidenecyclobutenes (DPCBs) **3** are alternative intriguing dimeric structures of phosphaallenes with loss of two H atoms. This dehydrogenative homocoupling of **1b** would provide the corresponding 1,2-bis(4-cyanophenyl)-3,4-diphosphinidenecyclobutene, but unfortunately **1b** was too unstable to isolate under the conditions in Scheme 2. Therefore, we examined an alternative synthesis of the CN-bearing DPCB derivative according to our recent procedures starting from **4**.[10,11]

Dibromophosphaethene **4** was allowed to react with butyllithium, 4-cyanobenzaldehyde, and chlorotrimethylsilane successively to afford the 2-bromo-1-phosphapropene **10b** in a moderate yield. According to the case of **10a**,[11] **10b** was subsequently treated with butyllithium and 1,2-dibromoethane, and the corresponding DPCB **3b** was obtained as yellow crystals. The ^{31}P NMR data of **3b** showed a lower-field chemical shift (δ_P 187) compared with **3a** (δ_P 170), due to the presence of the cyano groups (Scheme 3). Other NMR spectroscopic data of **3b** confirm the DPCB structure. On the other hand, mass spectra and elemental analysis of **3b** indicate inclusion of oxygen in the crystalline state, although attempted X-ray crystallography

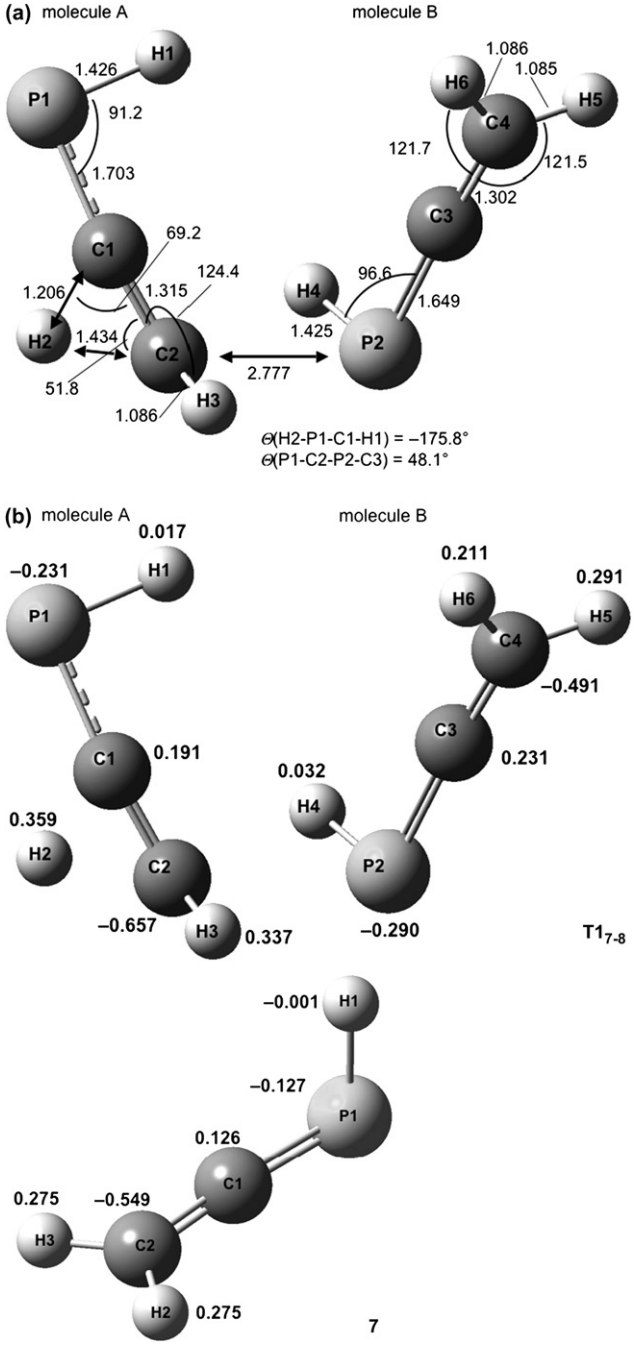


Figure 2. (a) Optimized geometry of $\mathbf{T1}_{7-8}$ (bond lengths: Å; bond angles: degree). (b) Mulliken charges of $\mathbf{T1}_{7-8}$ and **7**.

to investigate the O_2 absorption has thus far been unsuccessful. In addition to **3b**, a small amount of the cyanophenylphosphaallene **1b** was obtained in Scheme 3, indicating the decisive role of DBU to give the 1,4-diphosphafulvene **2b** in Scheme 2. In fact, a mixture of the isolated **1b** and DBU afforded **2b** (see Section 4). Although the detailed reaction mechanism from **10** to **3** has yet to be clarified, it is plausible that the products in Scheme 3 do not facilitate the [3+2] dimerization affording 1,4-diphosphafulvene **2**. Thus, the findings described in Schemes 2 and 3 would provide suitable processes for obtaining the [3+2] dimerization and the dehydrogenative homocoupling of **1**, respectively.

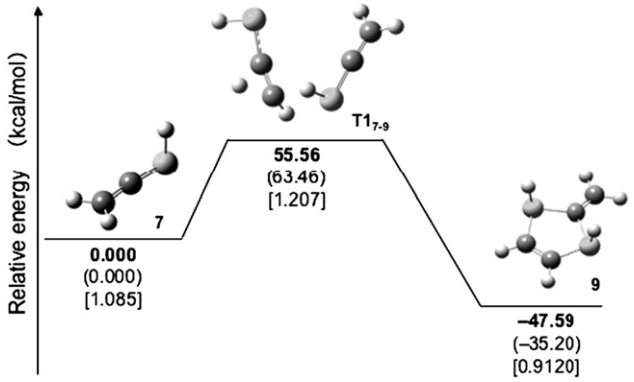


Figure 3. Calculated intermediate for head-to-tail [3+2] dimerization of **7** affording **9** (B3LYP/aug-cc-pVTZ). Values in bold face correspond to relative energies (kcal/mol). Values in parentheses display Gibbs free energies (kcal/mol at 298.15 K). Values in square brackets show dipole moments (Debye).

3. Conclusion

A 3-(4-cyanophenyl)-1-phosphaallene **1b**, an intermediary generated from a 2-bromo-1-phosphapropene **6b**, showed facile [3+2] dimerization in the presence of DBU affording **2b**. This is in sharp contrast to the case of **1a**, which was successfully prepared from **6a** and DBU. The DFT calculations characterize several plausible intermediary structures and pathways in the reaction from **1** to **2** and also indicate the cyano group effect to facilitate the dimerization. The physical properties of the cyano-containing 1,4-diphosphafulvene **2b** exhibited several different characteristics from those of **2a**. The formal dehydrogenative homocoupling product of **1b**, a 3,4-diphosphinidenecyclobutene **3b**, was prepared according to the recent DPCB synthetic procedures together with the cyano-bearing phosphaallene **1b**. Thus, from the effects of the cyanophenyl groups, several intriguing properties of phosphaallenes were derived in relation to the chemistry of

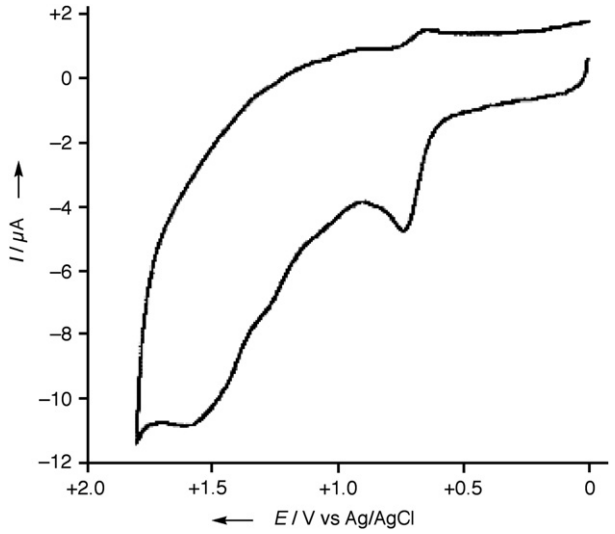
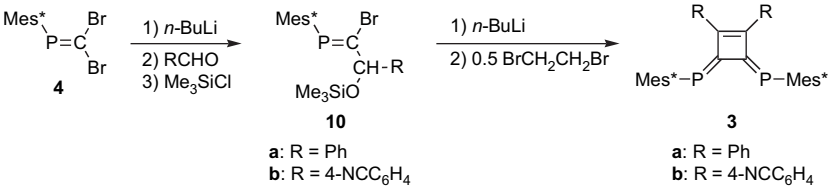


Figure 4. Cyclic voltammogram of **2b**. Conditions: 1 mM in dichloromethane; supporting electrolyte: 0.1 M tetrabutylammonium perchlorate (TBAP); working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: Ag/AgCl ($E_{1/2}$ (ferrocene/ferricinium)=+0.60 V) at 20 °C; scan rate: 50 mV s^{-1}.



Scheme 3.

1,4-diphosphafulvene and DPCB derivatives, including application for electron-transfer processes and catalysis.

4. Experimental section

4.1. General methods

All reactions were carried out under an argon atmosphere by means of the standard Schlenk techniques. All solvents employed were dried by appropriate methods. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance 400 spectrometer with Me_4Si (^{1}H, ^{13}C) and H_3PO_4 (^{31}P), respectively, as internal or external standard. Mass spectra were recorded on a Bruker APEX3 spectrometer. Electrochemical analyses were performed with a BAS-50W voltammetric analyzer. Compound **4** was prepared by the procedures described in the literature.[12]

4.2. Preparation of 6b

To a solution of **4** (400 mg, 0.893 mmol) in THF (25 mL) was added butyllithium (0.90 mmol, 1.4 M solution in hexane, 1 M=1 mol dm^{-3}) at −78 °C and after stirring for 10 min 4-cycanobenzyl bromide (9.0 mmol) in THF (5 mL) was added. After stirring for 15 min, the mixture was allowed to warm up to room temperature and the solvent was removed in vacuo. The residue was extracted with hexane and the organic layer was purified by column chromatography (SiO_2, hexane) to afford **6b** (190 mg, 47%). Colorless needles (EtOH), mp 114–116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (9H, s, *p*-*t*-Bu), 1.51 (18H, s, *o*-*t*-Bu), 4.23 (2H, d, $^{3}J_{PH}$=18.3 Hz, CH_2), 7.41–7.67 (6H, m, arom); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 31.8 (s, *p*-C*Me*$_3$), 33.2 (d, $^{4}J_{PC}$=6.7 Hz, *o*-C*Me*$_3$), 33.5 (s, *p*-*C*Me$_3$), 38.3 (s, *o*-*C*Me$_3$), 50.1 (d, $^{2}J_{PC}$=34.5 Hz, CH_2), 119.3 (s, CN), 122.6 (s, *m*-Mes*), 130.6 (s, *p*-C_6H_4), 132.1 (s, *m*-C_6H_4), 132.5 (s, *o*-C_6H_4), 137.8 (d, $^{1}J_{PC}$=53.0 Hz, *ipso*-Mes*), 144.0 (d, $^{3}J_{PC}$=12.7 Hz, *ipso*-C_6H_4), 151.5 (s, *p*-Mes*), 153.5 (d, $^{3}J_{PC}$=2.2 Hz, *o*-Mes*), 161.9 (d, $^{1}J_{PC}$=61.0 Hz, P=C); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 253.6; ESI-MS calcd for $C_{27}H_{35}{}^{79}BrNP$+Na 506.1583, found *m*/*z* 506.1582. Elemental analysis (%) calcd for $C_{27}H_{35}BrNP$ (484.45) C 66.94, H 7.28, N 2.89; found C 66.78, H 7.23, N 2.95. A trace amount (<5%) of the geometrical isomer of **6b** (δ_P 249.2, $^{3}J_{PH}$=9.1 Hz) was included.

4.3. Reaction of 6a with DBU

To a solution of **6a** (270 mg, 0.588 mmol) in THF (15 mL) was added DBU (1,8-diazabicyclo[5.4.0]undec-7-ene, 0.882 mmol) at 0 °C and the mixture was stirred for 30 min. The mixture was allowed to warm up to room temperature and the solvent was removed in vacuo. The residue was extracted with hexane and the organic layer was purified by column chromatography (SiO_2, hexane) to afford **1a**[17] (173 mg, 78%).

4.4. Reaction of 6b with DBU

To a solution of **6b** (64.6 mg, 0.133 mmol) in THF (5 mL) was added DBU (0.140 mmol) at 0 °C and the mixture was stirred for 30 min. The mixture was allowed to warm up to room temperature and the solvent was removed in vacuo. The residue was extracted with hexane and an aliquot of the solution was monitored by ^{31}P NMR to observe a signal due to **1b** [δ_P 80.2 (C_6D_6)] together with **2b** in a 1:2 ratio. The peak of **1b** disappeared within 1 h. The organic layer was purified by column chromatography (SiO_2, hexane/EtOAc 10:1) to afford **2b** (21 mg, 38%). Orange-red powder (hexane), mp 233–234 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (9H, s, *p*-*t*-Bu), 1.31 (9H, s, *p*-*t*-Bu), 1.54 (18H, s, *o*-*t*-Bu) 1.58 (18H, s, *o*-*t*-Bu), 6.40–6.44 (1H, m, CH), 6.44 (2H, d, $^{3}J_{HH}$=8.2 Hz, C_6H_4), 6.88 (1H, dd, $^{2}J_{PH}$=37.8 Hz, $^{3}J_{PH}$=12.2 Hz, CH), 7.09 (2H, d, $^{3}J_{HH}$=8.2 Hz, C_6H_4), 7.14 (2H, d, $^{3}J_{HH}$=8.2 Hz, C_6H_4), 7.38 (2H, d, $^{3}J_{HH}$=8.2 Hz, C_6H_4), 7.45 (2H, d, $^{4}J_{PH}$=2.4 Hz, Mes*), 7.51 (2H, d, $^{4}J_{PH}$=2.4 Hz, Mes*); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 31.5 (s, *p*-C*Me*$_3$), 31.6 (s, *p*-C*Me*$_3$), 33.8 (s, *o*-C*Me*$_3$), 34.3 (d, $^{4}J_{PC}$=4.7 Hz, *o*-C*Me*$_3$), 35.3 (s, *p*-*C*Me$_3$), 35.4 (s, *p*-*C*Me$_3$), 40.0 (d, $^{3}J_{PC}$=4.3 Hz, *o*-*C*Me$_3$), 40.2 (d, $^{3}J_{PC}$=5.1 Hz, *o*-*C*Me$_3$), 108.1 (s, CN), 110.6 (s, CN), 119.3 (s, C_{arom}), 119.8 (s, C_{arom}), 124.2 (s, *m*-Mes*), 124.8 (s, *m*-Mes*), 125.7 (d, $^{1}J_{PC}$=57.0 Hz, *ipso*-Mes*), 126.4 (d, $^{1}J_{PC}$=60.1 Hz, *ipso*-Mes*), 127.5 (dd, $^{4}J_{PC}$=6.0, 2.9 Hz, CH_{arom}), 127.8 (dd, $^{3}J_{PC}$=6.0 Hz, $^{4}J_{PC}$=2.9 Hz, CH_{arom}), 130.0 (dd, $^{1}J_{PC}$=9.9 Hz, $^{2}J_{PC}$=4.4 Hz, =C), 131.5 (dd, $^{1}J_{PC}$=46.2, 23.4 Hz, =C), 131.8 (s, CH_{arom}), 132.2 (s, CH_{arom}), 140.6 (t, $^{2}J_{PC}$=3.5 Hz, =CH), 142.2 (dd, $^{1}J_{PC}$=22.6 Hz, $^{2}J_{PC}$=10.3 Hz, =CH), 152.5 (s, *p*-Mes*), 153.4 (s, *p*-Mes*), 159.7 (s, *o*-Mes*), 159.9 (s, *o*-Mes*), 159.9 (s, C_{arom}), 160.0 (s, C_{arom}); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 54.5 (d, $^{2}J_{PP}$=35.2 Hz), 25.5 (d, $^{2}J_{PP}$=35.2 Hz); UV (CH_2Cl_2) λ_{max} ($\varepsilon\times10^{-3}$) 256 (33.6), 461 (4.7) nm; ESI-MS calcd for $C_{54}H_{68}N_2P_2$+Na 829.4750, found *m*/*z* 829.4747. Elemental analysis (%) calcd for $C_{54}H_{68}N_2P_2\cdot H_2O$ (825.09) C 78.61, H 8.55, N 3.40; found C 78.71, H 8.52, N 3.42.

4.5. Preparation of 10b

To a solution of **4** (553 mg, 1.23 mmol) in THF (20 mL) was added butyllithium (1.25 mmol) at −100 °C and the mixture was stirred for 15 min. The reaction mixture was mixed with a solution of 4-cyanobenzaldehyde (1.25 mmol) in THF

(7 mL) at −100 °C and stirred for 15 min. After warming up to room temperature, the mixture was treated with chlorotrimethylsilane (1.30 mmol) and was stirred for 1 h. The volatile materials were removed in vacuo and the residue was extracted with dichloromethane. The organic layer was concentrated and the residue was recrystallized from hexane to afford **10b** (392 mg, 56%). Colorless powder, mp 151–153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.19 (9H, s, $SiMe_3$), 1.33 (9H, s, *p*-*t*-Bu), 1.39 (9H, s, *o*-*t*-Bu), 1.49 (9H, s, *o*-*t*-Bu), 5.74 (1H, d, $^3J_{PH}$=12.8 Hz, CH), 7.38 (1H, s, Mes*), 7.41 (1H, s, Mes*), 7.60 (2H, d, $^3J_{HH}$=8.4 Hz, C_6H_4), 7.62 (2H, d, $^3J_{HH}$=8.4 Hz, C_6H_4); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 0.52 (s, $SiMe_3$), 31.7 (s, *p*-C*Me*$_3$), 33.0 (d, $^4J_{PC}$=6.8 Hz, *o*-C*Me*$_3$), 33.1 (d, $^4J_{PC}$=7.1 Hz, *o*-C*Me*$_3$), 35.4 (s, *p*-*C*Me$_3$), 38.2 (s, *o*-*C*Me$_3$), 38.4 (s, *o*-*C*Me$_3$), 79.8 (d, $^2J_{PC}$=38.5 Hz, CH), 111.7 (s, CN), 119.4 (s, C_{arom}), 122.6 (s, *m*-Mes*), 127.8 (s, CH_{arom}), 132.1 (s, CH_{arom}), 136.5 (d, $^1J_{PC}$=54.1 Hz, *ipso*-Mes*), 147.6 (d, $^3J_{PC}$=11.1 Hz, C_{arom}), 151.5 (s, *p*-Mes*), 153.4 (d, $^2J_{PC}$=2.3 Hz, *o*-Mes*), 153.9 (d, $^2J_{PC}$=2.3 Hz, *o*-Mes*), 165.8 (d, $^1J_{PC}$=64.0 Hz, P═C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 258.1; ESI-MS calcd for $C_{30}H_{43}{}^{79}$BrNPOSi+Na 594.1927, found *m*/*z* 594.1925. Elemental analysis (%) calcd for $C_{27}H_{35}$BrNPOSi (572.63) C 62.92, H 7.57, N 2.45; found C 63.14, H 7.41, N 2.45.

4.6. Preparation of 3b and 1b

To a solution of **10b** (0.165 mg, 0.288 mmol) in THF (10 mL) was added butyllithium (0.588 mmol) at −100 °C and the mixture was stirred for 15 min. Subsequently 1,2-dibromoethane (0.14 mmol) was added to the reaction mixture. The mixture was allowed to warm up to room temperature and stirred for 4 h. The volatile materials were removed in vacuo and the residue was extracted with dichloromethane. The organic layer was concentrated in vacuo and the residue was washed with hexane to give **3b** (60 mg, 52%). The hexane solution was concentrated and the residue was purified by column chromatography (SiO_2, hexane/EtOAc 100:1) to give **1b** (14 mg, 12%). **3b**: yellow powder (hexane), mp 297–300 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (18H, s, *p*-*t*-Bu), 1.53 (36H, s, *o*-*t*-Bu), 6.56 (4H, d, $^3J_{HH}$=8.3 Hz, C_6H_4), 7.10 (4H, d, $^3J_{HH}$=8.3 Hz, C_6H_4), 7.35 (4H, s, Mes*); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 32.0 (s, *p*-C*Me*$_3$), 33.7 (d, $^4J_{PC}$=2.0 Hz, *o*-C*Me*$_3$), 35.6 (s, *p*-*C*Me$_3$), 38.7 (s, *o*-*C*Me$_3$), 111.6 (s, CN), 118.8 (s, CH_{arom}), 122.4 (s, *m*-Mes*), 128.7 (s, C_{arom}), 131.9 (s, CH_{arom}), 134.6 (d, $^1J_{PC}$=27.1 Hz, *ipso*-Mes*), 136.1 (s, C_{arom}), 151.4 (s, *p*-Mes*), 153.3 (pt, ($^2J_{PC}$+$^3J_{PC}$)/2=6.8 Hz, C═C), 155.4 (s, *o*-Mes*), 174.7 (dd, $^1J_{PC}$=17.2, 8.7 Hz, P═C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 187.4; EI-MS *m*/*z* (rel intensity) 804 (M^+; 100%); ESI-MS calcd for $C_{54}H_{66}P_2$+Na 827.4593, found *m*/*z* 827.4591; calcd for $C_{27}H_{34}$NP+Na+4O 891.4390, found *m*/*z* 891.4381. Elemental analysis (%) calcd for $C_{54}H_{66}N_2P_2$+2O_2 (869.06) C 74.63, H 7.65, N 3.22; found C 74.18, H 7.90, N 3.40. **1b**: Colorless solid, mp 140–143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (9H, s, *p*-*t*-Bu), 1.64 (18H, s, *o*-*t*-Bu), 6.64 (1H, d, $^3J_{PH}$=26.4 Hz, ═CH), 7.37 (2H, d, $^3J_{HH}$=8.3 Hz, C_6H_4), 7.41 (2H, d, $^4J_{PH}$=1.8 Hz, Mes*), 7.55 (2H, d, $^3J_{HH}$=8.3 Hz, C_6H_4); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 31.7 (s, *p*-C*Me*$_3$), 33.8 (d, $^4J_{PC}$=7.0 Hz, *o*-C*Me*$_3$), 35.4 (s, *p*-*C*Me$_3$), 38.4 (s, *o*-*C*Me$_3$), 111.1 (s, CN), 112.0 (d, $^2J_{PC}$=10.6 Hz, ═CH), 119.3 (s, s, *p*-C_6H_4), 122.7 (s, *m*-Mes*), 128.8 (s, *m*-C_6H_4), 129.5 (s, *ipso*-C_6H_4), 132.6 (s, *o*-C_6H_4), 139.4 (d, $^1J_{PC}$=11.1 Hz, *ipso*-Mes*), 150.7 (s, *p*-Mes*), 154.3 (d, $^3J_{PC}$=3.6 Hz, *o*-Mes*), 240.4 (d, $^1J_{PC}$=25.0 Hz, P═C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 78.5; ESI-MS calcd for $C_{27}H_{34}$NP+Na 426.2321, found *m*/*z* 426.2320.

4.7. Reaction of 1b with DBU

To a solution of **1b** (10 mg, 25 μmol) in THF (3 mL) was added DBU (30 μmol) and the mixture was concentrated in vacuo. After 2 h, the residue was monitored by ^{31}P NMR to observe **2b** solely.

4.8. DFT calculations

Computations were performed with the Gaussian03 (revision C.02) quantum chemical program package.[18] In the DFT calculations, the functional of Becke3–Lee–Yang–Parr (B3LYP)[19,20] was employed. Geometry optimizations and harmonic vibrational frequency calculations were carried out with the B3LYP methods using aug-cc-pVTZ basis set. The harmonic vibrational frequencies of all stationary points were computed to characterize them as minima (all frequencies are real) or transition states (TSs; only one imaginary frequency). The reaction pathways were verified by IRC calculations.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.07.063.

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