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Simple and efficient preparation of sterically protected 1,4-diphosphafulvenes

Akitake Nakamura, Kozo Toyota and Masaaki Yoshifuji*

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba, Sendai 980-8578, Japan

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Abstract—A new synthetic method for sterically protected 1,4-diphosphafulvenes (2-methylene-2,3-dihydro-1*H*-[1,3]diphospholes) has been developed starting from (arylethynyl)phosphines and ca. 0.25 molar amount of butyllithium. The catalytic mechanism of the reaction is discussed based on the results of deuterium-labelling experiments.

1. Introduction

Heterocycles containing heavier main group elements have long been compounds of importance in many research fields such as medicinal chemistry and materials chemistry. For example, fulvenes and fulvalenes containing hetero atoms have been of interest. Since the discovery of the first organic metal, tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ), the quest for new synthetic metals and superconductors has been very active.[1] Thus, 2-methylene-2,3-dihydro-1*H*-[1,3]dichalcogenole derivatives have attracted much attention, because of their high π electron-donating properties.[2] In contrast, research on 2-methylene-2,3-dihydro-1*H*-[1,3]diphosphole has been limited until now.

Very recently, we have reported the formation of 2,6-diphenyl-1,4-bis(2,4,6-tri-*t*-butylphenyl)-1,4-diphospha-1,4-dihydrofulvene (or 2-benzylidene-4-phenyl-2,3-bis(2,4,6-tri-*t*-butylphenyl)-2,3-dihydro-1*H*-[1,3]diphosphole) (Chart 1, **1a**)[3] in 37% yield together with 3-phenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaallene (**2a**,[4] 5%) and a trace amount of 3,4-diphosphinidenecyclobutene derivative **3a** (hereafter, 3,4-*dip*hosphinidene*cyclo*-*but*ene, abbreviated as DPCB),[5] when (*Z*)-2-bromo-2-benzyl-1-(2,4,6-tri-*t*-butylphenyl)phosphaethene (**4**) was allowed to react with 2 molar amount of potassium *t*-butoxide. X-ray analysis of (*E*)-**1a** as well as a CV study was also reported.[3] Alternatively, Le Floch et al. reported the synthesis of a series of 1,4-diphosphafulvene derivative,[6] such as **5**, from a phosphorus version of the Arduengo carbene[7] and ketones or aldehydes. In the course of our continuing investigation of preparations and properties of DPCB derivatives,[8] we found that ethynylphosphines **6** (starting compounds in the syntheses of DPCB derivatives, Scheme 1) also afford **1** under certain conditions. Here, we report a simple and convenient method for the preparation of 1,4-diphosphafulvenes starting from ethynylphosphines bearing a bulky 2,4,6-tri-*t*-butylphenyl substituent[9] (abbreviated as Mes*).[10]

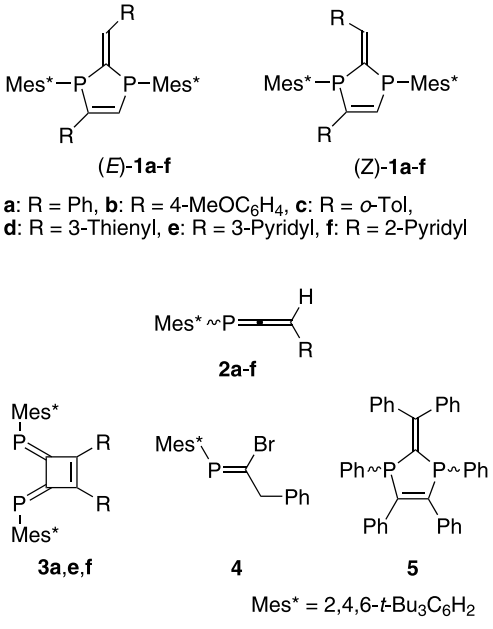

Chart 1.

Keywords: Phosphorus heterocycles; Phosphines; Phosphaallenes; Steric and strain effects.
* Corresponding author. Tel.: +81 22 795 6558; fax: +81 22 795 6562; e-mail: yoshifj@mail.tains.tohoku.ac.jp

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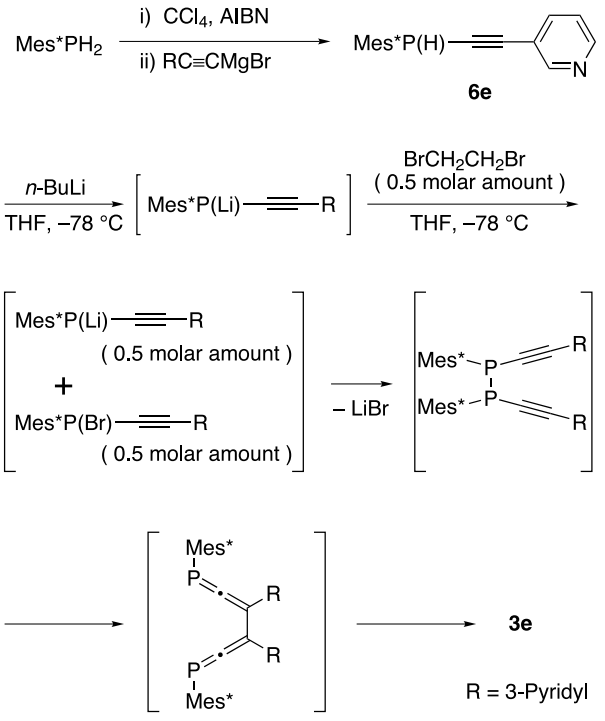
2. Results and discussion

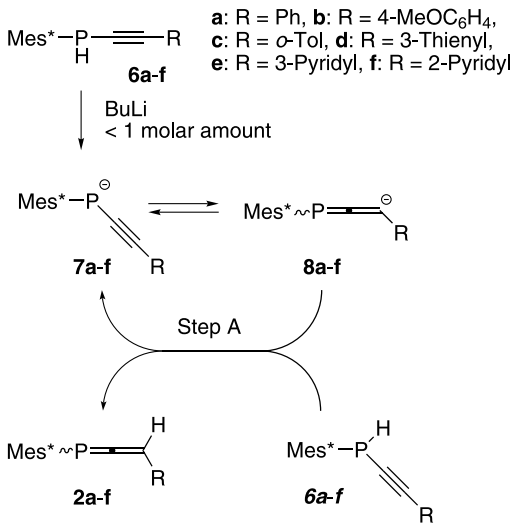
2.1. Preparation of 1,4-diphosphafulvenes

It has been established that a successive reaction of sterically protected ethynylphosphine **6** with *n*- or *t*-BuLi (1 molar amount) and 1,2-dibromoethane (0.5 molar amount) affords DPCB derivative **3**,[8a–f] as exemplified by the preparation of **3e**: Reaction of [(3-pyridyl)ethynyl]-phosphine **6e** with *n*-BuLi (1 molar amount) followed by reaction with 1,2-dibromoethane (0.5 molar amount) in THF at −78 °C affords the corresponding DPCB derivative **3e** in 21% yield based on the starting (2,4,6-tri-*t*-butylphenyl)-phosphine[11] (Scheme 1). In this reaction, it is likely that lithium [(3-pyridyl)ethynyl]phosphide reacts with 1,2-dibromoethane (0.5 molar amount) to form 0.5 molar amount of (bromo)[(3-pyridyl)ethynyl]phosphine. Coupling between the lithium phosphide and the (bromo)(pyridylethynyl)phosphine, followed by Cope rearrangement and electrocyclization, affords **3e**.



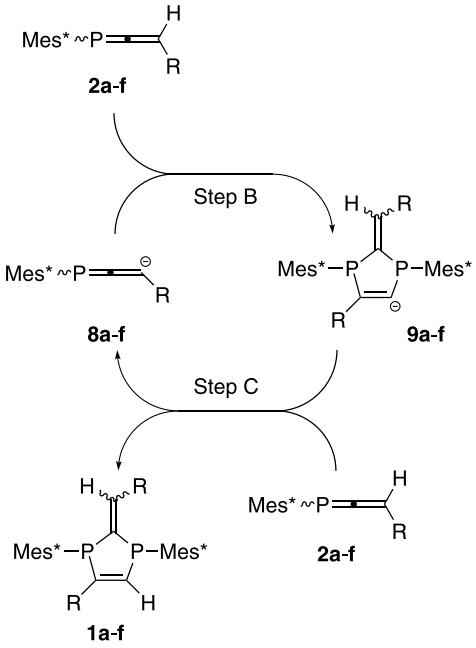
Scheme 1.

However, when a 2-pyridyl isomer **6f** (Scheme 2) was allowed to react with *n*-BuLi and 1,2-dibromoethane under similar conditions (crude **6f** was used because separation of **6f** from other products proved difficult), we found that **1f** instead of **3f** was formed by ^{31}P NMR spectroscopic monitoring, although only in trace yield due to difficulties in separation and purification [1.2% yield from starting Mes^*PH_2, **1f**: Orange solid, mp 237–239 °C (decomp.); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) $\delta=28.0$ (d, $^2J_{PP}=26.2$ Hz) and 47.1 (d, $^2J_{PP}=26.2$ Hz). HRMS (SIMS). Found *m/z* 759.4934. Calcd for $C_{50}H_{68}N_2P_2$: $M^+ + H$, 759.4930]. This striking contrast prompted us to investigate reaction conditions of **6a–e**[12] with *n*-BuLi which led to an

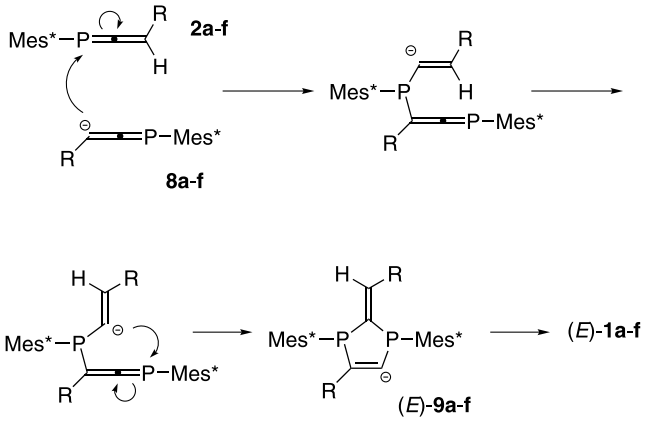


Scheme 2.

interesting discovery: Reactions of **6a–e** with *n*-BuLi (ca. 0.25 molar amount) in the absence of 1,2-dibromoethane at room temperature afforded **1a–e** (for purification of **1a–e**, see below), probably via a reaction between in situ prepared 1-phosphaallene **2a–e** and phosphaallenyl anion **8a–e** as shown in Schemes 2 and 3. This route includes three important steps A, B, and C. Step A (Scheme 2) is a very fast catalytic cycle, which involves, (i) partial lithiation of ethynylphosphine **6** with *n*-BuLi to form phosphide **7**, (ii) rearrangement of the anion **7** to the anion **8**,[13] and (iii) protonation of **8** by the starting ethynylphosphine **6** to form **2** and regenerate **8** (via **7**). Step B (Scheme 3) is a reaction between **2** (formed at Step A) and **8** to form **9**. Step B seems to proceed in a stepwise manner rather than a concerted manner, as shown in Scheme 4: compounds **2** and **8** first, react in a sterically less hindered manner, then bond rotation around the phosphorus-vinyl bond occurs, followed by cyclization in a sterically more congested manner to give



Scheme 3.



Scheme 4.

THF at room temperature yielded **1a** as a mixture of *E*- and *Z*-isomers [(*E*)-**1a**:(*Z*)-**1a**=2.7:1, determined by ^{31}P NMR spectroscopy]. We obtained (*E*)-**1a** in 55% isolated yield (Table 1, entry 2).

We then carried out a reaction of ethynylphosphine **6a** using 0.25 molar amount of *n*-BuLi. A clean reaction proceeded to afford **1a** in 70% isolated yield (Table 1, entry 1), which supports the above catalytic mechanism. Furthermore, we examined the protonation step of **9** with **2**, using deuterated 1-phosphaallene **2a**$_d$ (Chart 2). Reaction of **2a**$_d$ (97% D) with 0.26 molar amount of *t*-BuLi in THF at room temperature (generation of phosphaallenyllithium **8a**) yielded a dideuterated diphosphafulvene **1a**$_{d2}$ in 38% isolated yield with good D-incorporation, (91% D on the *exo*-methylene carbon and 73% D at the 3-position of the 1,4-dihydrofulvene ring) which also supports the mechanism via **8a** and **9a**$_d$ (Steps B and C). It should be mentioned that the expected maximum D-content at the 3-position is 74% D, based on the above mechanism, because 0.26 molar amount of *t*-BuLi were used to initiate the reaction by abstraction of D^+ from **2a**$_d$. It should also be noted that **2a** did not form **1a** in the absence of butyllithium.

Table 1. Preparation and oxidation potential of (*E*)-**1a–e**

Entry	Phosphine	R	*n*-BuLi[a]	Product	Yield[b]/%	$E_{1/2}$/V[c]
1	**6a**	Ph	0.25[d]	**1a**	70	0.02
2	**6a**	Ph	0.50	**1a**	55	
3	**6b**	4-MeOC$_6$H$_4$	0.25[d]	**1b**	46	−0.05
4	**6c**	*o*-Tol	0.30[d]	**1c**	38[e]	0.01[e]
5	**6d**	3-Thienyl	0.30[d]	**1d**	52	0.03
6	**6e**	3-Pyridyl	0.20[d]	**1e**	61	0.20

[a] Molar amount based on **6**.
[b] Yields were calculated taking the reaction mechanism into account (two molecules of **6** give one molecule of **1**).
[c] Conditions: 1 mM in CH_2Cl_2 with 0.1 M *n*-Bu_4NClO_4 as support electrolyte. Working electrode: glassy carbon; Counter electrode: Pt wire; Reference electrode: Ag/0.01 M $AgNO_3$ in acetonitrile with 0.1 M *n*-Bu_4NClO_4 [$E_{1/2}$ (Fc/Fc^+)=0.23 V]; Scan rate: 100 mV/s.
[d] Optimized data. The experiments were carried out using either 0.15, 0.20, 0.25, 0.30, 0.40, or 0.50 molar amounts of *n*-BuLi.
[e] Mixture of (*E*)- and (*Z*)-isomers.

(*E*)-**1** as a major product. The cyclization is likely a kinetically controlled reaction, due to the difficulty of inversion of the sp^2-carbanion.

First, we thought **1** is simply a quenched product of **9**, but the mechanism turned out to be not so straightforward according to the following experimental results. Step C (Scheme 3) is considered to operate as the final step of this mechanism. Intermediate **9** appears to be protonated by the remaining 1-phosphaallene **2**, before work-up (see below), and regenerates the phosphaallenyl anion **8**.

Attempted deuteration of intermediate **9a** by addition of methanol-d_4 failed, suggesting that the protonation of **9** occurs before addition of methanol-d_4. Thus, a catalytic amount of **8** formed in situ is expected to convert two molecules of phosphaallene **2** to **1**. Indeed, the reaction of ethynylphosphine **6a** with 0.5 molar amount of *n*-BuLi in

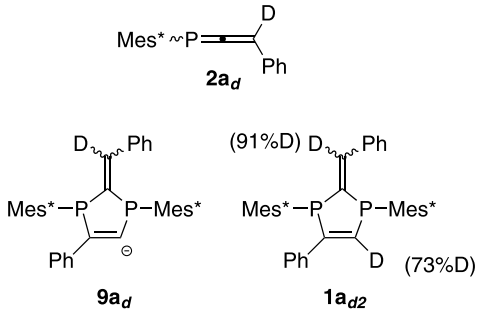


Chart 2.

2.2. Cyclic voltammogram of 1,4-diphosphafulvenes

Results of cyclic voltammetric measurements of compounds **1b–e** in dichloromethane are shown in Table 1, together with that of **1a**.[3] All compounds showed reversible

We then carried out a reaction of ethynylphosphine **6a** using 0.25 molar amount of *n*-BuLi. A clean reaction proceeded to afford **1a** in 70% isolated yield (Table 1, entry 1), which supports the above catalytic mechanism. Furthermore, we examined the protonation step of **9** with **2**, using deuterated 1-phosphaallene **2a**$_d$ (Chart 2). Reaction of **2a**$_d$ (97% D) with 0.26 molar amount of *t*-BuLi in THF at room temperature (generation of phosphaallenyllithium **8a**) yielded a dideuterated diphosphafulvene **1a**$_{d2}$ in 38% isolated yield with good D-incorporation, (91% D on the *exo*-methylene carbon and 73% D at the 3-position of the 1,4-dihydrofulvene ring) which also supports the mechanism via **8a** and **9a**$_d$ (Steps B and C). It should be mentioned that the expected maximum D-content at the 3-position is 74% D, based on the above mechanism, because 0.26 molar amount of *t*-BuLi were used to initiate the reaction by abstraction of D^+ from **2a**$_d$. It should also be noted that **2a** did not form **1a** in the absence of butyllithium.

The scope and limitations of this methodology were then investigated. Reactions of ethynylphosphines **6b–e** afforded (*E*)-**1b–e** and (*Z*)-**1b–e** (Table 1). Although (*E*)-**1c** and (*Z*)-**1c** were not separated from the mixture, compounds (*E*)-**1b**,**d**,**e** were isolated. However, when ethynylphosphines **6** bearing primary alkyl (R=*n*-Bu), secondary alkyl (R=cyclohexyl), tertiary alkyl (R=*t*-Bu), trimethylsilyl, (*t*-butyldimethylsilyloxy)methyl, or *p*-(trifluoromethyl)-phenyl were employed, the results were unsatisfactory due to partial formation of the corresponding phosphaallenes.

It should be noted that Table 1 (entries 1, 3–6) shows optimized result with respect to the molar amount of butyllithium. When less butyllithium than the optimized amount was used, recovery of the starting ethynylphosphine **6** increased. When more butyllithium than the optimized amount was used, yield of the by-product **2** increased.

oxidation peaks. Among the five 1,4-diphosphafulvenes, **1b** showed the lowest oxidation potential and the order was **1b** < **1c** < **1a** < **1d** < **1e**. This tendency indicates that electron-donating substituents lower the oxidation potentials. The compounds **1a–e** showed relatively good electron-donating activities with E_{ox} values ranging from −0.05 to 0.20 V. This relatively large range for the E_{ox} values of **1** indicates significant effects of the substituent at the 2- or 6-positions on the redox properties of **1** and the tendency found here may become a good guide for developing new material containing the diphosphafulvene structure.

3. Conclusion

In summary, we have developed a new synthetic methodology for diphosphafulvene via sterically protected 1-phosphaallene intermediates. The reaction mechanism turned out interestingly to involve phosphaallenyllithium as catalyst. As the experimental procedure is simple and the starting ethynylphosphines are easily prepared from (2,4,6-tri-*t*-butylphenyl)phosphine, these facts merit this preparation method.

4. Experimental

4.1. General

Melting points were measured on a Yanagimoto MP-J3 micro melting point apparatus and were uncorrected. NMR spectra were recorded on a Bruker Avance-400 or a Bruker AM-600 spectrometer. IR spectra were obtained on a Horiba FT-300 spectrometer. FT-ICR-MS spectra were measured on a Bruker APEX III spectrometer. Cyclic voltammograms were recorded on a BAS-CV-50W voltammetric analyzer under nitrogen. Reactions were performed under an argon atmosphere while work-up was carried out in air, unless otherwise specified.

4.1.1. 2,6-Diphenyl-1,4-bis(2,4,6-tri-*t*-butylphenyl)-1,4-diphospha-1,4-dihydrofulvene (1a). To a solution of **6a** (182.7 mg, 0.483 mmol) in THF (1.0 mL) was added 0.075 mL of *n*-BuLi (1.60 M solution in hexane) at room temperature and the resulting mixture was stirred overnight. The solvent was removed under reduced pressure. Column chromatography (SiO_2) of the residue provided a mixture of (*E*)-**1a** and (*Z*)-**1a**. To this mixture was added acetone and insoluble (*E*)-**1a**[3] was obtained (127.2 mg, 70% yield) by filtration.

Compound (*Z*)-**1a**. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ= 48.9 (d, $^2J_{PP}$=19.5 Hz) and 25.2 (d, $^2J_{PP}$=19.5 Hz).

4.1.2. 2,6-Bis(4-methoxyphenyl)-1,4-bis(2,4,6-tri-*t*-butylphenyl)-1,4-diphospha-1,4-dihydrofulvene (1b). To a solution of **6b** (122.4 mg, 0.300 mmol) in THF (0.6 mL) was added 0.050 mL of *n*-BuLi (1.54 M solution in hexane) at room temperature and the resulting mixture was stirred overnight. The solvent was removed under reduced pressure and a residual mixture of (*E*)-**1b** and (*Z*)-**1b** was obtained. To the residue was added acetone and insoluble (*E*)-**1b** was obtained (56.7 mg, 46% yield) by filtration.

Compound (*E*)-**1b**. Yellow solid, mp 185–188 °C (decomp.); ^1H NMR (600 MHz, $CDCl_3$) δ=1.35 (18H, s, *p*-*t*-Bu), 1.64 (36H, br, *o*-*t*-Bu), 3.70 (3H, s, OCH_3), 3.75 (3H, s, OCH_3), 6.28 (2H, d, $^3J_{HH}$=8.4 Hz, *o*-arom.), 6.43 (2H, d, $^3J_{HH}$=8.4 Hz, *m*-arom.), 6.45 (1H, dd, $^3J_{PH}$=19.8, 6.6 Hz, C*H*Anis), 6.66 (2H, d, $^3J_{HH}$=8.4 Hz, *m*-arom.′), 6.69 (1H, dd, $^2J_{PH}$=37.2 Hz and $^3J_{PH}$=13.2 Hz, PC*H*), 7.07 (2H, d, $^3J_{HH}$=8.4 Hz, *o*-arom.′), and 7.51 (4H, br, *m*-Mes*); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ=31.2 (s, *p*-C*Me*$_3$), 31.3 (s, *p*-C*Me*$_3$), 33.5 (br, *o*-C*Me*$_3$), 34.0 (br, *o*-C*Me*$_3$), 34.7 (s, *p*-*C*Me$_3$), 34.9 (s, *p*-*C*Me$_3$), 39.6 (d, $^3J_{PC}$=4.5 Hz, *o*-*C*Me$_3$), 39.8 (br, *o*-*C*Me$_3$), 55.0 (s, OCH_3), 55.1 (s, OCH_3), 113.1 (s, Anis), 113.2 (s, Anis), 123.5 (br, *m*-Mes*), 124.8 (dd, $^1J_{PC}$=22.6 Hz, $^2J_{PC}$=10.6 Hz, P*C*H), 127.9 (dd, $^3J_{PC}$=4.5 Hz, $^4J_{PC}$=1.5 Hz, Anis), 128.9 (dd, $^4J_{PC}$=5.3 Hz, 2.3 Hz, Anis), 129.2 (d, $^1J_{PC}$=61.9 Hz, *ipso*-Mes*), 129.3 (dd, $^1J_{PC}$=61.9 Hz, $^3J_{PC}$=3.0 Hz, *ipso*-Mes*), 130.9 (dd, $^2J_{PC}$=21.9 Hz, $^3J_{PC}$=2.3 Hz, *ipso*-Anis), 131.3 (d, $^3J_{PC}$=4.5 Hz, *ipso*-Anis), 131.4 (dd, $^1J_{PC}$= 42.3 Hz, 34.7 Hz, P*C*P), 134.6 (dd, $^2J_{PC}$=27.2 Hz, 24.1 Hz, *C*HAnis), 142.1 (t, J_{PC}=14.3 Hz, P*C*Anis), 150.6 (s, *p*-Mes*), 150.6 (s, *p*-Mes*), 151.6 (s, *o*-Mes*), 151.6 (s, *o*-Mes*), 157.5 (s, Anis), and 158.5 (s, Anis); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ=53.8 (d, $^2J_{PP}$=22.5 Hz) and 23.1 (d, $^2J_{PP}$=22.5 Hz); UV–Vis (hexane) 256 (log ε 4.54), 295 (sh, 4.45), and 406 nm (3.92); IR (KBr) ν/cm^{-1} 2958, 2906, 2833, 1601, 1504, 1466, 1392, 1360, 1294, 1248, 1211, 1176, 1117, 1038, 874, 804, and 754. HRMS (ESI). Found *m*/*z* 816.5162. Calcd for $C_{54}H_{74}O_2P_2^+$: M^+, 816.5159. Found: C, 74.97; H, 8.91%. Calcd for $C_{54}H_{74}O_2P_2\cdot 3H_2O$: C, 74.45; H, 9.26%.

Compound (*Z*)-**1b**. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ= 49.3 (d, $^2J_{PP}$=17.9 Hz) and 25.6 (d, $^2J_{PP}$=17.9 Hz).

4.1.3. 2,6-Bis(2-methylphenyl)-1,4-bis(2,4,6-tri-*t*-butylphenyl)-1,4-diphospha-1,4-dihydrofulvene (1c). Compound **6c** (138.4 mg, 0.353 mmol) in THF (0.7 mL) was converted to **1c**, by a method similar to that of **1b**, by using 0.070 mL of *n*-BuLi (1.54 M solution in hexane). The residue was recrystallized from hexane to give 52.4 mg (38% yield) of a mixture of (*E*)-**1c** and (*Z*)-**1c**.

Compound (*E*)-**1c**. ^1H NMR (600 MHz, $CDCl_3$) δ=1.28 (18H, s, *p*-*t*-Bu), 1.59 (36H, br, *o*-*t*-Bu), 1.87 (3H, s, CH_3), 2.56 (3H, s, CH_3), 6.14 (1H, dd, $^3J_{PH}$=16.8 Hz, 7.2 Hz, C*H*Tol), 6.20 (1H, br d, arom.), 6.42 (1H, t, $^3J_{HH}$=7.5 Hz, arom.), 6.48 (1H, dd, $^2J_{PH}$=36.9 Hz, $^3J_{PH}$=13.5 Hz, PC*H*), 6.76 (1H, t, $^3J_{HH}$=7.2 Hz, arom.), 6.84 (1H, d, $^3J_{HH}$= 7.2 Hz, arom.), 6.96 (1H, t, $^3J_{HH}$=7.2 Hz, arom.′), 7.05 (1H, t, $^3J_{HH}$=7.5 Hz, arom.′), 7.18 (1H, d, $^3J_{HH}$=7.8 Hz, arom.′), 7.36 (1H, d, $^3J_{HH}$=7.2 Hz, arom.′), 7.36 (2H, br, *m*-Mes*), and 7.47 (2H, s, *m*-Mes*); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ=19.9 (s, CH_3), 21.4 (s, CH_3), 31.1 (s, *p*-C*Me*$_3$), 31.3 (s, *p*-C*Me*$_3$), 33.4 (br, *o*-C*Me*$_3$), 33.9 (br, *o*-C*Me*$_3$), 34.7 (s, *p*-*C*Me$_3$), 34.9 (s, *p*-*C*Me$_3$), 39.4 (d, $^3J_{PC}$=3.0 Hz, *o*-*C*Me$_3$), 39.5 (d, $^3J_{PC}$=3.0 Hz, *o*-*C*Me$_3$), 123.4 (br, *m*-Mes*), 125.0 (s, Tol), 125.2 (s, Tol), 125.4 (s, Tol), 125.7 (d, $^4J_{PC}$=9.1 Hz, Tol), 126.2 (s, Tol), 126.8 (d, $^1J_{PC}$=57.3 Hz, *ipso*-Mes*), 128.4 (dd, $^3J_{PC}$=7.5 Hz, $^4J_{PC}$=4.5 Hz, Tol), 129.0 (s, Tol), 131.0 (t, $^2J_{PC}$=7.5 Hz, *C*HTol), 131.1 (s, Tol), 131.6 (d, $^1J_{PC}$=67.9 Hz, *ipso*-Mes*), 131.6 (dd, $^1J_{PC}$=21.9 Hz, $^2J_{PC}$=11.3 Hz, P*C*H),

134.7 (s, Tol), 134.9 (dd, $^{1}J_{PC}=42.3$ Hz, 30.2 Hz, P*C*P), 135.5 (s, Tol), 136.3 (m, *ipso*-Tol), 138.7 (d, $^{2}J_{PC}=21.1$ Hz, *ipso*-Tol), 141.3 (dd, $^{1}J_{PC}=22.6$ Hz, $^{2}J_{PC}=15.1$ Hz, P*C*Tol), 150.8 (s, *p*-Mes*), and 151.5 (s, *o*-Mes*); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) $\delta=64.1$ (d, $^{2}J_{PP}=26.6$ Hz) and 24.2 (d, $^{2}J_{PP}=26.6$ Hz). HRMS [ESI, mixture of (*E*)-**1c** and (*Z*)-**1c**]. Found *m*/*z* 784.5265. Calcd for $C_{54}H_{74}P_2^+$: M^+, 784.5260.

Compound (*Z*)-**1c**. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) $\delta=$ 53.4 (d, $^{2}J_{PP}=20.7$ Hz) and 26.1 (d, $^{2}J_{PP}=20.7$ Hz).

4.1.4. 2,6-Bis(3-thienyl)-1,4-bis(2,4,6-tri-*t*-butylphenyl)-1,4-diphospha-1,4-dihydrofulvene (1d). Compound **6d** (151.3 mg, 0.395 mmol) in THF (0.8 mL) was converted to (*E*)-**1d** (78.0 mg, 52% yield), by a method similar to that of **1b**, by using 0.075 mL of *n*-BuLi (1.54 M solution in hexane).

Compound (*E*)-**1d**. Yellow solid, mp 203–205 °C (decomp.); ^{1}H NMR (600 MHz, $CDCl_3$) $\delta=1.38$ (9H, s, *p*-*t*-Bu), 1.39 (9H, s, *p*-*t*-Bu), 1.63 (36H, br, *o*-*t*-Bu), 5.33 (1H, s, Thienyl), 6.04 (1H, s, Thienyl′), 6.45 (1H, d, $^{3}J_{HH}=$ 4.8 Hz, Thienyl), 6.73 (1H, dd, $^{3}J_{PH}=17.7$ Hz, 4.5 Hz, C*H*,Thienyl), 6.76 (1H, dd, $^{2}J_{PH}=37.8$ Hz, $^{3}J_{PH}=13.2$ Hz, PC*H*), 6.93 (1H, dd, $^{3}J_{HH}=4.8$ Hz, $^{4}J_{HH}=2.4$ Hz, Thienyl), 7.09–7.14 (2H, m, Thienyl′), 7.53 (2H, br, *m*-Mes*), and 7.56 (2H, br, *m*-Mes*); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) $\delta=31.2$ (s, *p*-C*Me*$_3$), 31.4 (s, *p*-C*Me*$_3$), 33.4 (br, *o*-C*Me*$_3$), 33.9 (d, $^{4}J_{PC}=4.5$ Hz, *o*-C*Me*$_3$), 34.8 (s, *p*-*C*Me$_3$), 35.0 (s, *p*-*C*Me$_3$), 39.5 (d, $^{3}J_{PC}=4.5$ Hz, *o*-*C*Me$_3$), 39.9 (br, *o*-*C*Me$_3$), 121.4 (t, $J_{PC}=3.8$ Hz, Thienyl), 121.5 (dd, $^{4}J_{PC}=6.0$ Hz, 4.5 Hz, Thienyl), 123.4 (s, Thienyl), 123.4 (br, *m*-Mes*), 124.2 (s, Thienyl), 125.5 (dd, $^{1}J_{PC}=22.6$ Hz, $^{2}J_{PC}=10.6$ Hz, P*C*H), 125.8 (d, $J_{PC}=4.5$ Hz, Thienyl), 127.5 (dd, $^{1}J_{PC}=59.6$ Hz, $^{3}J_{PC}=2.3$ Hz, *ipso*-Mes*), 128.3 (s, Thienyl), 129.2 (d, $^{1}J_{PC}=63.4$ Hz, *ipso*-Mes*), 129.3 (t, $^{2}J_{PC}=26.4$ Hz, *C*H,Thienyl), 133.1 (dd, $^{1}J_{PC}=41.5$ Hz, 37.0 Hz, P*C*P), 137.2 (t, $J_{PC}=11.3$ Hz, P*C*Thienyl), 138.9 (dd, $^{2}J_{PC}=23.4$ Hz, $^{3}J_{PC}=2.3$ Hz, *ipso*-Thienyl), 139.6 (d, $^{3}J_{PC}=6.0$ Hz, *ipso*-Thienyl), 151.3 (s, *p*-Mes*), 151.3 (s, *p*-Mes*), 152.2 (s, *o*-Mes*), and 152.2 (s, *o*-Mes*); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) $\delta=48.0$ (d, $^{2}J_{PP}=24.9$ Hz) and 19.7 (d, $^{2}J_{PP}=24.9$ Hz); UV–Vis (hexane) 255 (log ε 4.55), 285 (sh, 4.40), and 400 nm (3.92); IR (KBr) ν/cm^{-1} 2960, 2906, 2868, 1595, 1558, 1392, 1360, 1236, 1211, 1120, 874, 854, and 768. HRMS (ESI). Found *m*/*z* 768.4079. Calcd for $C_{48}H_{66}P_2S_2^+$: M^+, 768.4076.

Compound (*Z*)-**1d**. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) $\delta=$ 46.6 (d, $^{2}J_{PP}=15.2$ Hz) and 23.8 (d, $^{2}J_{PP}=15.2$ Hz).

4.1.5. 2,6-Bis(3-pyridyl)-1,4-bis(2,4,6-tri-*t*-butylphenyl)-1,4-diphospha-1,4-dihydrofulvene (1e). Compound **6e** (160.2 mg, 0.422 mmol) in THF (0.8 mL) was converted to **1e** (78.0 mg, 52% yield), by a method similar to that of **1b**, by using 0.055 mL of *n*-BuLi (1.54 M solution in hexane).

Compound (*E*)-**1e**. Yellow solid, mp 207–210 °C (decomp.); ^{1}H NMR (600 MHz, $CDCl_3$) $\delta=1.28$ (9H, s, *p*-*t*-Bu), 1.29 (9H, s, *p*-*t*-Bu), 1.56 (18H, br, *o*-*t*-Bu), 1.59 (18H, br, *o*-*t*-Bu), 6.27 (1H, d, $^{3}J_{HH}=7.8$ Hz, Pyr), 6.36 (1H, dd, $^{3}J_{PH}=$ 16.8 Hz, 6.0 Hz, C*H*Pyr), 6.60 (1H, dd, $^{3}J_{HH}=7.5$ Hz, 5.1 Hz, Pyr), 6.80 (1H, dd, $^{2}J_{PH}=37.5$ Hz, $^{3}J_{PH}=12.3$ Hz, PC*H*), 6.99 (1H, dd, $^{3}J_{HH}=7.5$ Hz, 5.1 Hz, Pyr′), 7.25 (1H, d, $^{3}J_{HH}=7.2$ Hz, Pyr′), 7.41 (2H, s, *m*-Mes*), 7.49 (2H, s, *m*-Mes*), 7.96 (1H, s, Pyr), 8.08 (1H, d, $^{3}J_{HH}=4.2$ Hz, Pyr), 8.34 (1H, d, $^{3}J_{HH}=4.2$ Hz, Pyr′), and 8.51 (1H, s, Pyr′); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) $\delta=31.1$ (s, *p*-C*Me*$_3$), 31.2 (s, *p*-C*Me*$_3$), 33.3 (br, *o*-C*Me*$_3$), 33.9 (d, $^{4}J_{PC}=4.5$ Hz, *o*-C*Me*$_3$), 34.7 (s, *p*-*C*Me$_3$), 34.9 (s, *p*-*C*Me$_3$), 39.5 (d, $^{3}J_{PC}=4.5$ Hz, *o*-*C*Me$_3$), 39.6 (d, $^{3}J_{PC}=4.5$ Hz, *o*-*C*Me$_3$), 122.7 (s, Py), 123.6 (br, *m*-Mes*), 124.1 (br, *m*-Mes*), 126.0 (d, $^{1}J_{PC}=54.3$ Hz, *ipso*-Mes*), 127.4 (d, $^{1}J_{PC}=58.9$ Hz, *ipso*-Mes*), 128.0 (dd, $^{1}J_{PC}=22.6$ Hz, $^{2}J_{PC}=10.6$ Hz, P*C*H), 129.7 (dd, $^{2}J_{PC}=30.2$ Hz, 22.6 Hz, *C*HPyr), 132.4 (dd, $^{4}J_{PC}=7.5$ Hz, 3.0 Hz, Pyr), 133.4–133.7 (m, *ipso*-Py), 133.5 (m, Py), 137.5 (dd, $^{1}J_{PC}=41.5$ Hz, 37.0 Hz, P*C*P), 139.3 (t, $J_{PC}=15.8$ Hz, P*C*Pyr), 145.8 (s, Py), 147.7 (t, $J_{PC}=3.0$ Hz, Pyr), 147.8 (s, Py), 149.7 (t, $^{4}J_{PC}=3.8$ Hz, Pyr), 151.4 (s, *p*-Mes*), 151.5 (s, *p*-Mes*), 152.4 (s, *o*-Mes*), and 152.4 (s, *o*-Mes*); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) $\delta=54.2$ (d, $^{2}J_{PP}=31.0$ Hz) and 25.1 (d, $^{2}J_{PP}=31.0$ Hz); UV–Vis (hexane) 256 (log ε 4.59), 290 (sh, 4.38), and 419 nm (3.95); IR (KBr) ν/cm^{-1} 2960, 2906, 2868, 1591, 1527, 1473, 1398, 1360, 1238, 1209, 1182, 1124, 1024, 876, 791, and 708. HRMS (ESI). Found *m*/*z* 759.4926. Calcd for $C_{50}H_{68}N_2P_2^+$: MH^+, 759.4930. Found: C, 77.26; H, 8.99; N, 3.62%. Calcd for $C_{50}H_{68}N_2P_2\cdot H_2O$: C, 77.28; H, 9.08; N, 3.61%.

Compound (*Z*)-**1e**. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) $\delta=$ 50.3 (d, $^{2}J_{PP}=21.7$ Hz) and 24.6 (d, $^{2}J_{PP}=21.7$ Hz).

4.1.6. 1,2-Bis(3-pyridyl)-3,4-bis[(2,4,6-tri-*t*-butylphenyl)-phosphinidene]cyclobutene (3e). A mixture of (2,4,6-tri-*t*-butylphenyl)phosphine (275.4 mg, 0.989 mmol) and AIBN (10.3 mg, 0.0627 mmol) in CCl_4 (3 mL) was refluxed for 4 h. The solvent was removed under reduced pressure and 2 mL of THF was added. In a separate flask, 1.01 mmol of ethylmagnesium bromide (0.96 M solution in THF) was added to a THF (2 mL) solution of 3-ethynylpyridine (103.2 mg, 1.00 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 10 min., allowed to warm to room temperature, and added to the THF solution of chloro(2,4,6-tri-*t*-butylphenyl)phosphine prepared above. The resulting mixture was stirred for 10 min and passed through short silica-gel column using EtOAc as eluent. Removal of the solvent afforded [(3-pyridyl)ethynyl]phosphine **6e**, which was used for the following reactions as obtained. To a solution of **6e** in THF (2 mL) was added 1.00 mmol of *n*-BuLi (1.59 M solution in hexane) at −78 °C and the resulting solution was stirred for 10 min, 1,2-dibromoethane (0.0499 mmol) was added, and stirred for 10 min. The resulting mixture was then allowed to warm to room temperature and stirred for 1 h. The solvent was removed under reduced pressure, 2 mL of toluene was added to the residue, and the toluene solution was refluxed for 30 min. Removal of the solvent under vacuum followed by column chromatographic separation (SiO_2/hexane–EtOAc) provided 79.6 mg of **3e** [21% based on the starting (2,4,6-tri-*t*-butylphenyl)phosphine].

Yellow solid, mp 266–269 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta=1.37$ (18H, s, *p*-*t*-Bu), 1.55 (36H,

br, *o*-*t*-Bu), 6.50 (2H, d, $^{3}J_{HH}=8.0$ Hz, Pyr), 6.71 (2H, dd, $^{3}J_{HH}=8.0$ Hz, 4.8 Hz, Pyr), 7.33 (4H, s, *m*-Mes*), 7.86 (2H, s, Pyr), and 8.22 (2H, d, $^{3}J_{HH}=4.8$ Hz, Pyr); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) $\delta=32.0$ (s, *p*-C*Me*$_3$), 33.7 (br, *o*-C*Me*$_3$), 35.5 (s, *p*-*C*Me$_3$), 38.7 (s, *o*-*C*Me$_3$), 122.3 (s, arom.), 123.3 (s, arom.), 128.1 (s, arom.), 134.5 (pseudo t, $J_{PC}=28.3$ Hz, *ipso*-Mes*), 135.2 (s, Pyr), 148.8 (s, arom.), 148.9 (s, arom.), 151.1 (s, *o*-Mes*), 152.7 (pseudo t, $J_{PC}=7.0$ Hz, P=C–*C*), 155.2 (s, *o*-Mes*), and 175.6 (dd, $^{1}J_{PC}=18.4$ Hz, $^{2}J_{PC}=8.1$ Hz, P=C); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) $\delta=179.6$; UV–Vis (hexane) 246 (log ε 4.45), 325 (4.53), and 377 nm (sh, 4.03); IR (KBr) ν/cm^{-1} 2954, 1591, 1471, 1400, 1363, and 1242. HRMS (ESI). Found *m*/*z* 757.4773. Calcd for $C_{50}H_{67}N_2P_2^+$: MH^+, 757.4774.

4.2. Reaction of 2a$_d$ with *t*-butyllithium

To a solution of **2a**$_d$ (127.7 mg, 0.337 mmol, 97% D) in THF (1.0 mL) was added 0.088 mmol (0.26 molar amount) of *t*-BuLi (1.46 M solution in pentane) and the resulting solution was stirred overnight. The solvent was evaporated under reduced pressure. ^{31}P NMR spectrum of the residue showed signals due to (*E*)- and (*Z*)-diphosphadihydrofulvenes as well as the starting **2a**$_d$. To the residue was added acetone and the insoluble (*E*)-**1a**$_{d2}$ was obtained (48.2 mg, 38% yield) by filtration. D content of the product was determined by ^{1}H NMR spectroscopy.

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