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Synthesis and properties of air-stable 1,3-diphosphacyclobutane-2,4-diyls and the related compounds

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Abstract

A kinetically stabilized phosphaalkyne bearing a bulky Mes* (2,4,6-tri-*t*-butylphenyl) group is useful compound to prepare an enormous number of highly stable 1,3-diphosphacyclobutane-2,4-diyls through reactions with a lithium reagent and an electrophile. By utilizing this synthetic protocol, we prepared several non-symmetrical 1,3-diphosphacyclobutane-2,4-diyls in which the substituents on the phosphorus are different. Furthermore, we succeeded in preparation and characterization of novel air-tolerant symmetrical 2,4-bis(2,4,6-tri-*t*-butylphenyl)-1,3-diphosphacyclobutane-2,4-diyls bearing the identical alkyl substituents on the phosphorus atoms. Structures and properties of the 1,3-diphosphacyclobutane-2,4-diyls indicate characters as singlet ground-state carbon centered biradicals. In addition to those biradicals, we succeeded in preparation and isolation of a novel P-heterocyclic air-stable neutral radical as well as a P-heterocyclic cation radical.
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1. Introduction

Chemistry of stable biradicals is one of the most remarkable subjects in molecular science and it has been developed together with main-group organic chemistry [1]. In 1995, Niecke and co-workers synthesized the first 1,3-diphosphacyclobutane-2,4-diyl (**1**) as a room-temperature tolerant singlet biradical via an oxidative coupling of an anionic phosphaethene intermediate [2]. By utilizing a unique B–B bond breaking reaction, Bertrand and co-workers succeeded in isolation and characterization of a P,B-based singlet biradical **2**, which is also stable at room temperature [3]. These particular biradicals including phosphorus have stimulated to synthesize novel exotic compounds leading to new materials.

Multiple bonds of heavier main group elements are important chemical species in main group chemistry and we have studied chemistry of low-coordinated phosphorus compounds [4] to find out various reactions and molecular structures [5–7]. In the course of our research on such low-coordinated phosphorus compounds, we have found a useful synthetic method for 2,4-bis(2,4,6-tri-*t*-butylphenyl)-1,3-diphosphacyclobutane-2,4-diyls of biradical type (**3**) by use of a kinetically stabilized phosphaalkyne [Mes*C≡P: **4**] (Mes* = 2,4,6-tri-*t*-butylphenyl) [8–10]. Although Niecke's biradical **1** carries two sterically protecting Mes* groups, our biradical **3** demonstrates exceptional stability toward air at room temperature due to the effective stabilizing cooperation of an electronically perturbing phosphino group and the Mes* groups. Furthermore, our synthetic protocol for 1,3-diphosphacyclobutane-2,4-diyls assures us of wide scope for preparation of varieties of P-heterocyclic biradical compounds simply by employing various nucleophiles and electrophiles [9,10].

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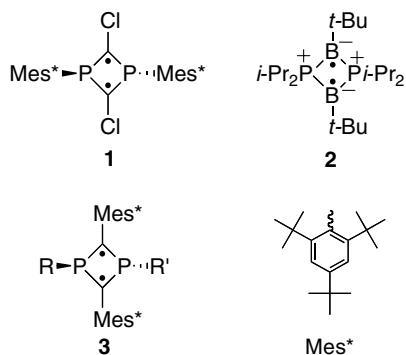
We describe here preparation of several novel 1,3-diphosphacyclobutane-2,4-diyls carrying different or identical substituents on the phosphorus atoms, which leads to profound discussion of structural properties of the biradical compounds. Additionally, we have succeeded in preparation and isolation of a novel P-heterocyclic monoradical and the properties are presented and discussed.

2. Results and discussion

2.1. Synthesis and physical properties of air-stable 1,3-diphosphacyclobutane-2,4-diyls

The kinetically stabilized phosphaalkyne 4 was prepared from 2,2-dibromo-1-(2,4,6-tri-t-butylphenyl)-1-phosphaethene [Mes*P = CBr$_2$] by utilizing the nickel-mediated [1,2] migration of the phosphorus version of Fritsch–Buttenberg–Wiechell rearrangement as described in our previous reports [7,8]. Reaction of 4 with 0.5 equivalents of t-butyllithium afforded the corresponding four-membered anionic intermediates 5 through a [2+2] cyclization of a 1,3-diphosphabuta-1,3-diene skeleton [8–11]. The room-temperature stable P-heterocyclic anions 5 were allowed to react with alkyl or acyl halides to afford the unsymmetrically substituted 1,3-diphosphacyclobutane-2,4-diyls 3a–e through the P-alkylation pathway [8–10] (Scheme 1). The P-heterocyclic biradicals 3a–e can be handled in air at room temperature, indicating successful cooperation of kinetic protection by the Mes* group with thermodynamic perturbation by the phosphino group. Table 1 displays ^{31}P NMR and UV–Vis spectroscopic data of the isolated biradicals 3. In ^{31}P NMR, the unsymmetrical P-heterocyclic biradicals 3a–e displayed typical AB signals, and the t-BuP phosphorus showed lower chemical shifts rather than the other P atom. Interestingly, electron-withdrawing

substituents caused lower-field shift of the t-BuP phosphorus as shown in 3c and 3e together with reduction of the abnormally large $^2J_{PP}$ couplings, probably indicating peculiar physicochemical properties of the singlet ground state biradical system composed of P and C. On the other hand, in ^{13}C NMR, the C$_{sp2}$ atoms of 3c and 3e showed relatively higher field shifts [3c: $\delta_C = 97.7$] [9] together with larger $^1J_{PC}$ couplings [3c: 25.0, 16.7 Hz] [9] compared with those for 3a, 3b, and 3d, which might be due to effects of the electron-withdrawing substituent groups [12]. The UV–Vis absorption data of 3a–e indicate that electron-withdrawing benzoyl group reduces the HOMO–LUMO gap, whereas a similar electronegative perfluoroalkyl group does not cause red shift of the P,C-biradical system. Such physical properties of 3e might indicate unique σ-electron withdrawing and π-electron donating effect of fluorine atom [13]. The unsymmetrical biradicals bearing benzyl or perfluoroalkyl group (3b, 3e) showed relatively high stability and survived in air for a couple of months. A P-heterocyclic biradical bearing a long alkyl chain such as 3d has a lower melting point than the other biradical derivatives without apparent decomposition.

To obtain more information by comparison with Niecke's biradical 1, we attempted to prepare novel biradicals carrying symmetrical phosphino groups. The P$_2$C$_2$ biradicals that we previously reported have a deformed lozenge structure to display shorter and phosphaalkene-like P–C distances together with longer and almost P–C single bond distances in the four-membered ring, which has been critically argued to characterize our compounds as biradical structures [8–10]. Therefore, an attempt was made to obtain novel biradicals, which are comparable with 1 by use of our synthetic strategy. Phosphaalkyne 4 was allowed to react with 0.5 equivalents of t-butyllithium, n-butyllithium, and methyllithium, and the generated anionic intermediates were treated with t-butyl iodide, n-butyl chloride, and iodomethane, respectively, to give the desired symmetrical biradicals 3f–h in moderate yields (Scheme 2). Table 1 also displays the ^{31}P NMR and UV–Vis spectroscopic data of symmetrical 3f–h indicating that the absorptions data are almost the same as those of 1,3-diphosphacyclobutane-2,4-diyls carrying unsymmetrical dialkyl substituents such as 3a, 3b, and 3d. On the other hand, the absorption spectra of 3f–h show a considerable red shift compared with that of 1 (478 nm) [2], probably indicating effects of the aromatic Mes* substituents attached on the radical sp^2 C atoms. The symmetrical biradicals 3f–h can be handled in air for a couple of days without any significant decomposition and the ^{13}C NMR showed analogous data to those of 3a, 3b, and 3d.

2.2. Electrochemistry of 1,3-diphosphacyclobutane-2,4-diyls

Table 2 shows electrochemical data of 3e–h together with the previously reported data of 3a [8]. Compounds 3a and 3e were employed to discuss effects of substituents on redox properties of unsymmetrical 1-t-butyl-1,3-diphos-
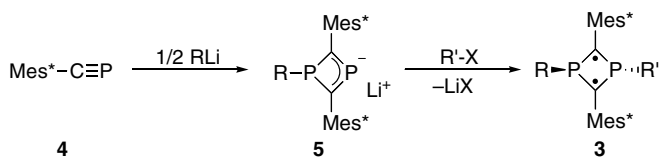
Scheme 1.

Table 1
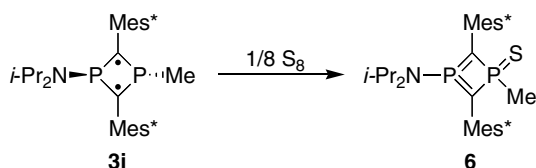^{31}P NMR and UV–Vis data of 1,3-diphosphacyclobutane-2,4-diyls **3**

Compound	R	R′	δ_P (RP)[a]	δ_P (R′P) [a]	$^2J_{PP}$/Hz[a]	λ_{max} ($\varepsilon \times 10^3$)/nm[b]	Ref.
3a	t-Bu	Me	55.9	−11.3	362.8	612 (1.5)	[8]
3b	t-Bu	CH$_2$Ph	58.1	0.6	334.8	610 (1.7)	[10]
3c	t-Bu	C(O)Ph	73.2	25.2	215.1	664 (1.5)	[9]
3d	t-Bu	C$_{18}$H$_{37}$	55.6	3.7	333.2	606 (1.9)	[d]
3e	t-Bu	C$_3$F$_7$	96.8	−12.4	213.7	587 (1.3)	[d]
3f	t-Bu	t-Bu	39.3		–	574 (1.7)	[d]
3g	n-Bu	n-Bu	13.8		–	595 (1.8)	[d]
3h	Me	Me	0.5[c]		–	590 (1.0)	[d]

[a] In CDCl$_3$.
[b] In hexanes.
[c] See Ref. [14].
[d] This work.

Scheme 2.

Table 2
Redox potentials of symmetrical 1,3-diphosphacyclobutane-2,4-diyls[a]

Compound	R	R′	$E_{1/2}^{ox}$	E_p^{ox}	E_p^{red}
3a	t-Bu	Me	+0.35	+1.56	−0.70
3e	t-Bu	C$_3$F$_7$	+0.85	+1.11	−0.70
3f	t-Bu	t-Bu	+0.28	+1.60	−0.77
3g	n-Bu	n-Bu	+0.44	+1.55	−0.83
3h	Me	Me	+0.39[b]	+1.55	−0.81

[a] *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}.
[b] Irreversible.

phacyclobutane-2,4-diyl derivatives. The perfluoroalkyl biradical **3e** in dichloromethane showed a higher 1st oxidation potential compared with that of **3a**, whereas its 2nd oxidation potential was lower than the corresponding data of **3a** [8]. Similarly to the discussion on the absorption spectra, such electrochemical properties of **3e** might indicate the σ-electron withdrawing and π-electron donating effect of fluorine atoms [13]. On the other hand, reduction potential of **3e** (−0.70 V) does not appear to be influenced by the perfluoroalkyl group.

Electrochemical properties of symmetrical 1,3-diphosphacyclobutane-2,4-diyls **3f**–**h** were examined to compare with those of the unsymmetrical 1,3-diphosphacyclobutane-2,4-diyls (Table 2). Compound **3f** showed considerably low 1st oxidation potential suggesting effects of the electron-donating two t-butyl groups, whereas the corresponding potential of **3g** would indicate inferior electron-donating ability of n-butyl group. The irreversible

1st oxidation wave of **3h** would indicate instability of the corresponding cation radical upon oxidation. The 2nd oxidation potentials and reduction peaks of **3f**–**h** are similar. The lower reduction potentials of **3f**–**h** relative to that of **3a** might indicate differences between unsymmetrical and symmetrical 1,3-diphosphacyclobutane-2,4-diyls. Indeed, the unsymmetrical 1,3-diphosphacyclobutane-2,4-diyl **3a** and **3b** bear considerably shorter P–C$_{sp2}$ bonds (*vide infra*) [8,10], which might increase electron-accepting ability as observed in phosphaalkenes [4,15].

2.3. X-ray structures of 1,3-diphosphacyclobutane-2,4-diyls

Fig. 1 demonstrates a molecular structure of an unsymmetrical 1,3-diphosphacyclobutane-2,4-diyl bearing a perfluoroalkyl group **3e** (Table 3). Although quality of the solution is not necessarily enough to discuss the metric parameters in detail, its typical structural characters are almost the same as the previously analyzed structures of **3a** and **3b** [8,10]. The P$_2$C$_2$ four-membered ring is almost planar, and the carbon atoms in the ring show the sp^2 hybridized structure. The phosphorus atom carrying t-butyl group shows less-pyramidalized structure [Σ(P1) = 350.7°] compared with the other phosphorus [Σ(P2) = 310.9°], and correspondingly, the t-BuP–C$_{sp2}$ distances in the four-membered ring are shorter. The two Mes* rings make the mean angle to the biradical plane of 59.3 and 60.7°, respectively, probably to minimize steric congestion. In contrast to the structure of **3a** and **3b**, one of the two Mes* groups distorted toward the t-Bu group on the P1 atom and the other Mes* repels from the t-Bu group.

Fig. 2 shows structure of a symmetrical 1,3-diphosphacyclobutane-2,4-diyl bearing methyl groups (Table 3). Two independent molecules are observed and the two molecules showed somewhat intermolecular contact based on the CH–π interaction between the PMe group and the Mes* aromatic ring. One of the two independent molecules is shown in Fig. 2. The rhombus P$_2$C$_2$ ring and the P–C1 distances correspond to Niecke's symmetrical biradical **1** [P–C$_{sp2}$ 1.749(3), 1.750(2) Å] [2]. On the other hand, sum of the bond angles around the C1 atom of **3g** indicated
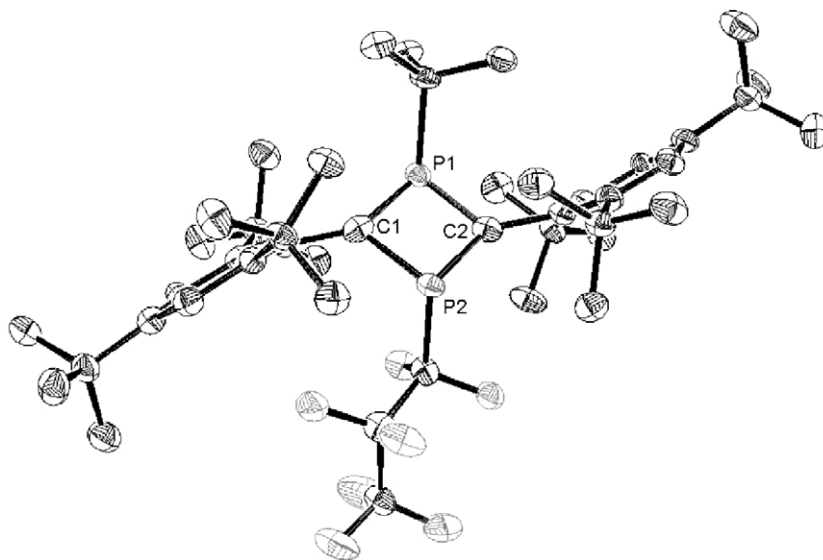
Fig. 1. An ORTEP drawing of the molecular structure of **3e**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–C1 1.722(9), P1–C2 1.722(9), P1–C$_{t\text{-}Bu}$ 1.906(9), P2–C1 1.799(9), P2–C2 1.806(9), P2–C$_{C3F7}$ 1.915(9), C1–C$_{Mes^*}$ 1.49(1), C2–C$_{Mes^*}$ 1.49(1), C1–P1–C2 95.6(4), C1–P1–C$_{t\text{-}Bu}$ 131.2(4), C2–P1–C$_{t\text{-}Bu}$ 123.9(4), C1–P2–C2 90.1(4), C1–P2–C$_{C3F7}$ 112.5(4), C2–P2–C$_{C3F7}$ 108.3(4), P1–C1–P2 86.9(4), P1–C1–C$_{Mes^*}$ 145.7(7), P2–C1–C$_{Mes^*}$ 126.7(7), C2–P2–C$_{C3F7}$ 108.3(4), P1–C2–P2 86.7(4), P1–C2–C$_{Mes^*}$ 128.9(7), P2–C2–C$_{Mes^*}$ 139.6(7), Θ(P1–C1–P2–C2) 5.9(4).

Table 3
Crystal data for **3e** and **3h**

Compound	**3e**	**3h**
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$ (#14)	$P\bar{1}$ (#2)
a (Å)	13.466(3)	16.1829(5)
b (Å)	17.698(6)	12.6555(7)
c (Å)	19.498(5)	10.4394(7)
α (°)	90	71.862(1)
β (°)	108.72(2)	88.973(3)
γ (°)	90	67.956(3)
V (Å^3)	4400(2)	1871.3(2)
$2\theta_{max}$ (°)	55	55
T (K)	133	133
Z	4	2
Observed reflections	22214	14921
Unique reflections	8528	7845
R_{int}	0.080	0.041
R_1 ($I > 2\sigma(I)$)	0.115	0.074
R_W (all data)	0.301	0.155

planar sp^2 carbon [Σ(C1) = 359.6°], which is different from the corresponding data of **1** [Σ(C1) = 347.3°] [2]. Taking the theoretically calculated structures into consideration [2,16], the experimentally obtained metric parameters of **3h** demonstrate properties as a singlet ground state biradical [17]. The two Mes* rings make the angle of 57.3° to the four membered biradical plane eventually to stabilize the inherent unstable structure by the steric bulk.

2.4. Reactions of 1,3-diphosphacyclobutane-2,4-diyls

We previously reported that **3a** caused P–C bond cleavage to afford phosphaalkyne **4** upon heating [8,10]. Similarly, thermolysis of 1,3-diphosphacyclobutane-2,4-diyls

bearing alkyl groups (**3b**, **3d–h**) afforded **1** together with considerable amount of unidentified products. A 1,3-diphosphacyclobutane-2,4-diyl bearing acyl group **3c** showed a ring-expansion reaction including the Arbuzov-type reaction to afford a 1-oxo-1H-[1,3]diphosphole [9].

On the other hand, 1,3-diphosphacyclobutane-2,4-diyl **3i** carrying an amino group showed relatively various reactivity [9]. Indeed, sulfurization of **3i** afforded a cyclic dimethylenephosphorane **6** in a moderate yield. Structure of **6** was characterized by spectroscopic data and X-ray crystallography (quality of the X-ray analysis was not acceptable to discuss the structure). The data of **6** are comparable to the oxygen analog **7** [9] (Scheme 2).

2.5. Preparation of P-heterocyclic monoradicals

The preparation protocol for 1,3-diphosphacyclobutane-2,4-diyls **3** as shown in Scheme 1 could be successfully utilized for formation of stable 1,3-diphosphacyclobuten-4-yl radicals [18]. A heterocyclic anion **5** (R = t-Bu), prepared according to Scheme 1, was oxidized by iodine to afford the corresponding neutral radical **8** as deep red crystals almost quantitatively (Scheme 3).

The metric parameters of **8** obtained by X-ray crystallography display several characteristics of the P$_2$C$_2$ cyclic monoradical [18]. The four-membered ring is almost planar and the conformation of the two Mes* group is comparable to those of 2,4-bis(2,4,6-tri-t-butylphenyl)-1,3-diphosphacyclobutane-2,4-diyls. The sp^2-phosphorus atom includes the contracted P–C$_{sp2}$ bonds whereas the t-BuP phosphorus shows normal P–C$_{sp2}$ single bond lengths together with the pyramidalized structure. The EPR data of **8** as well as theoretical calculations for the model molecule characterized the spin properties [18].
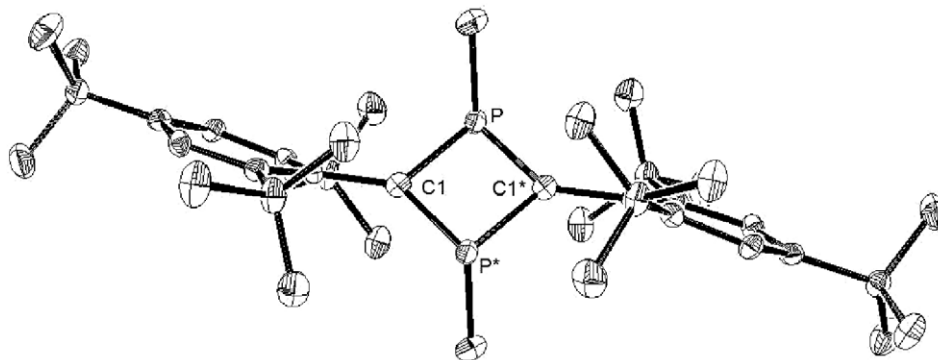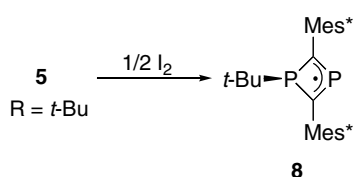
Fig. 2. An ORTEP drawing of the molecular structure of **3h**. Two independent molecules are observed and one of them is displayed. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P–C1 1.745(3), P–C1* 1.749(3), P–C_{Me} 1.819(4), C1–C_{Mes*} 1.488(4), C1–P–C1* 92.4(1), C1–P–C_{Me} 119.4(2), C1*–P–C_{Me} 118.6(2), P–C1–P* 87.6(1), P–C1–C_{Mes*} 141.3(2), P*–C1–C_{Mes*} 130.7(2), Θ(P–C1–P*–C1*) 0.0.

Scheme 3.

The 1,3-diphosphacyclobutane-2,4-diyls **3** prepared from **4** showed considerable π-electron donating ability as described in Section 2.2 [8]. Indeed, we succeeded in generation, EPR observation, and characterization by utilizing theoretical calculations of a cation radical **9** through one-electron oxidation procedures with tris(4-brimophenyl)ammoniumyl hexachloroantimonate [19].
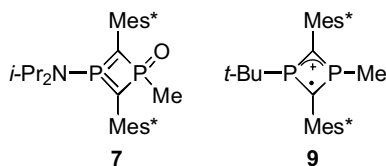
3. Conclusion

We have demonstrated syntheses, characterization, and properties of the air-stable unsymmetrical and symmetrical 1,3-diphosphacyclobutane-2,4-diyls of singlet biradical type (**3**). Each biradical **3** showed unique characters and may lead to novel exotic P-heterocyclic materials. By utilizing the synthetic procedure for **3**, we have succeeded in obtaining novel air-stable P-heterocyclic neutral radical **7** together with cation radical **8**.

4. Experimental

4.1. General

All manipulations were carried out under an argon atmosphere by means of 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 AVANCE400 spectrometer in CDCl$_3$ with Me$_4$Si (^{1}H, ^{13}C) and H$_3$PO$_4$ (^{31}P), respectively, as an internal or external standard. Melting points were measured on a Yanagimoto MP-J3 apparatus without correction. Elemental analyses were performed in the Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University. X-Ray diffraction data were collected on a Rigaku RAXIS-IV imaging plate diffractometer with graphite-monochromated MoK$_\alpha$ radiation ($\lambda = 0.71070$ Å). The structure was solved by direct methods (SIR92) [20], expanded using Fourier techniques (DIRDIF94) [21]. Structure solution, refinement, and graphical representation were carried out using the teXsan package [22]. Compound **4** was synthesized according to our previous report [8].

4.2. Preparation of 3: typical procedures

To a solution of **4** (300 mg, 1.0 mmol) in THF (8 mL) was added t-butyllithium (0.57 mmol, 0.41 mL of a 1.4 M solution in pentane) at −78 °C and the mixture was stirred for 15 min. The mixture was then allowed to warm to room temperature and allowed to react with haloalkanes (0.90 mmol) for 2 h or perfluoropropyl iodide for 12 h. The solvent was removed in vacuo. The residual material was extracted with dichloromethane and washed with ethanol to afford **3**. Recrystallization from dichloromethane afforded the single crystals.

Compound **3d**: 90% yield, blue-violet needles (CH$_2$Cl$_2$), mp 89–91 °C; ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) $\delta = 55.6$ (d, $^2J_{PP} = 333.2$ Hz, t-BuP), 3.7 (d, $^2J_{PP} = 333.2$ Hz, C$_{18}$H$_{37}$P); ^{1}H NMR (400 MHz, CDCl$_3$) $\delta = 7.39$ (2H, d, $^5J_{PH} = 1.2$ Hz, m-Mes*), 7.24 (2H, s, m-Mes*), 2.36–2.28 (2H, m, CH$_2$P), 1.63 (18H, s, o-t-Bu), 1.62 (18H, s, o-t-Bu), 1.32 (18H, s, p-t-Bu), 1.30–1.26 (32H, brs, CH$_2$), 0.91 (3H, t, $^3J_{HH} = 6.8$ Hz, CH$_3$), 0.70 (9H, d, $^3J_{PH} = 13.6$ Hz, t-BuP); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) $\delta = 150.5$ (t, $^2J_{PC} = 8.4$ Hz, ipso-Mes*), 148.5 (d, $^3J_{PC} = 10.2$ Hz, o-Mes*), 145.0 (s, p-Mes*), 134.1 (d, $^3J_{PC} =$

5.7 Hz, o-Mes*), 122.8 (d, $^4J_{PC}$ = 1.8 Hz, m-Mes*), 120.4 (s, m-Mes*), 109.6 (dd, $^1J_{PC}$ = 13.5 Hz, $^1J_{PC}$ = 9.8 Hz, C_{sp2}), 47.0 (dd, $^1J_{PC}$ = 52.5 Hz, $^1J_{PC}$ = 13.4 Hz, PCMe$_3$), 38.8 (s, o-CMe$_3$), 37.9 (s, o-CMe$_3$), 35.3 (s, CH$_2$), 34.9 (s, p-CMe$_3$), 33.9 (s, o-CMe$_3$), 33.8 (s, o-CMe$_3$), 32.3 (s, p-CMe$_3$), 31.9 (s, CH$_2$), 31.5 (d, $^1J_{PC}$ = 10.2 Hz, PCH$_2$CH$_2$), 30.1 (s, CH$_2$), 30.0 (d, $^3J_{PC}$ = 1.9 Hz, PCH$_2$CH$_2$CH$_2$), 29.8 (d, $^2J_{PC}$ = 4.6 Hz, PCMe_3), 29.5 (s, CH$_2$), 26.3 (d, $^2J_{PC}$ = 13.0 Hz, PCH$_2$), 23.1 (s, CH$_2$), 14.5 (s, CH$_2$); UV–Vis (hexanes) λ_{max} ($\varepsilon \times 10^3$) 329 (18.8), 383 (15.8), 606 (1.9); EA Found: C, 80.32; H, 11.74%, Calc. for C$_{60}$H$_{104}$P$_2 \cdot$ 0.1CH$_2$Cl$_2$, C, 80.57; H 11.72%.

Compound **3e**: 37% yield, blue-violet prisms (CH$_2$Cl$_2$), mp 158–160 °C (decomp); ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ = 96.8 (d, $^2J_{PP}$ = 213.7 Hz, t-BuP), −12.4 (d, $^2J_{PP}$ = 213.7 Hz, C$_3$F$_7$P); ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.41 (2H, s, m-Mes*), 7.29 (2H, s, m-Mes*), 1.62 (18H, s, o-t-Bu), 1.60 (18H, s, o-t-Bu), 1.31 (18H, s, p-t-Bu), 0.82 (9H, d, $^3J_{PH}$ = 15.6 Hz, t-BuP); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ = 152.4 (dd, $^2J_{PC}$ = 9.4 Hz, $^2J_{PC}$ = 6.3 Hz, $ipso$-Mes*), 149.2 (d, $^3J_{PC}$ = 11.6 Hz, o-Mes*), 146.5 (d, $^5J_{PC}$ = 2.2 Hz, p-Mes*), 131.3 (d, $^3J_{PC}$ = 6.1 Hz, o-Mes*), 123.2 (d, $^4J_{PC}$ = 2.5 Hz, m-Mes*), 121.3 (s, m-Mes*), 97.1 (pt, ($^1J_{PC}$ + $^1J_{PC}$)/2 = 28.4 Hz, C_{sp2}), 50.5 (d, $^1J_{PC}$ = 38.4 Hz, PCMe$_3$), 39.0 (s, o-CMe$_3$), 37.8 (s, o-CMe$_3$), 35.2 (s, p-CMe$_3$), 33.7 (s, o-CMe$_3$), 33.6 (s, o-CMe$_3$), 31.7 (s, p-CMe$_3$), 29.2 (pt, ($^2J_{PC}$ + $^4J_{PC}$)/2 = 2.5 Hz, PCMe_3) (C$_3$F$_7$ carbon atoms were not determined); UV–Vis (hexanes) λ_{max} ($\varepsilon \times 10^3$) 307 (11.8), 365 (13.5), 587 (1.3); EA Found: C 67.13, H 8.50%, Calc. for C$_{45}$H$_{67}$F$_7$P$_2$, C 67.31, H 8.41%.

Compound **3f**: 67% yield, blue-violet powder (CH$_2$Cl$_2$), mp 150–152 °C (decomp); ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ = 39.3; ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.35 (4H, s, m-Mes*), 1.68 (36H, s, o-t-Bu), 1.33 (18H, s, p-t-Bu), 1.00 (18H, pt, ($^3J_{PH}$ + $^5J_{PH}$)/2 = 6.8 Hz, t-BuP); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ = 149.0 (t, $^3J_{PC}$ = 6.5 Hz, o-Mes*), 144.8 (s, p-Mes*), 135.5 (t, $^2J_{PC}$ = 2.8 Hz, $ipso$-Mes*), 122.4 (s, m-Mes*), 109.2 (t, $^1J_{PC}$ = 4.2 Hz, C_{sp2}), 46.4 (pt, ($^1J_{PC}$ + $^3J_{PC}$)/2 = 20.5 Hz, PCMe$_3$), 38.6 (s, o-CMe$_3$), 35.1 (t, $^5J_{PC}$ = 3.7 Hz, o-CMe$_3$), 34.9 (s, p-CMe$_3$), 31.9 (s, p-CMe$_3$), 31.1 (pt, ($^2J_{PC}$ + $^4J_{PC}$)/2 = 5.2 Hz, PCMe_3); UV–Vis (hexanes) λ_{max} ($\varepsilon \times 10^3$) 340 (18.1), 385 (13.4), 574 (1.7); HRMS (ESI) Found: m/z 690.5413, Calc. For C$_{46}$H$_{76}$P$_2$, 690.5417. EA Found: C, 78.84; H, 10.85%, Calc. for C$_{46}$H$_{76}$P$_2 \cdot$ 0.1CH$_2$Cl$_2$, C, 79.15, H, 10.98%.

Compound **3g**: 58% yield, blue-violet plates (CH$_2$Cl$_2$), mp 130–131 °C (decomp); ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ = 13.8; ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.43 (4H, s, m-Mes*), 2.10 (4H, pt, ($^2J_{PH}$ + $^4J_{PH}$)/2 = 7.3 Hz, PCH$_2$), 1.64 (36H, s, o-t-Bu), 1.36 (18H, s, p-t-Bu), 1.10–1.02 (8H, m, CH$_2$), 0.65 (6H, t, $^3J_{HH}$ = 6.9 Hz, Me); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ = 150.5 (t, $^3J_{PC}$ = 6.5 Hz, o-Mes*), 145.8 (t, $^5J_{PC}$ = 2.8 Hz, p-Mes*), 133.5 (t, $^2J_{PC}$ = 2.8 Hz, $ipso$-Mes*), 121.9 (s, m-Mes*), 110.1 (t, $^1J_{PC}$ = 4.7 Hz, C_{sp2}), 38.3 (s, o-CMe$_3$), 35.1 (s, p-CMe$_3$),

34.4 (t, $^5J_{PC}$ = 4.2 Hz, o-CMe$_3$), 31.9 (s, p-CMe$_3$), 31.0 (pt, ($^1J_{PC}$ + $^3J_{PC}$)/2 = 17.6 Hz, PCH$_2$), 26.8 (pt, ($^2J_{PC}$ + $^4J_{PC}$)/2 = 5.6 Hz, PCH$_2$CH$_2$), 24.1 (pt, ($^3J_{PC}$ + $^5J_{PC}$)/2 = 5.5 Hz, PCH$_2$CH$_2$CH$_2$), 13.9 (s, Me); UV–Vis (hexanes) λ_{max} ($\varepsilon \times 10^3$) 328 (23.0), 372 (12.1), 595 (1.8); EA Found: C, 78.42; H, 11.20%, Calc. for C$_{46}$H$_{76}$P$_2 \cdot$ 0.2CH$_2$Cl$_2$, C, 78.37; H, 10.88%.

Compound **3h**: 72% yield, blue-violet plates (CH$_2$Cl$_2$), mp 180–184 °C (decomp); ^{31}P{^{1}H} NMR (162 MHz, C$_7$D$_8$) δ = 0.5; ^{1}H NMR (400 MHz, C$_7$D$_8$) δ = 7.70 (4H, s, m-Mes*), 1.78 (36H, s, o-t-Bu), 1.40 (18H, s, p-t-Bu), 1.33 (6H, s, Me); ^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$) δ = 150.8 (t, $^3J_{PC}$ = 6.8 Hz, o-Mes*), 145.9 (t, $^5J_{PC}$ = 2.1 Hz, p-Mes*), 132.2 (t, $^3J_{PC}$ = 3.3 Hz, $ipso$-Mes*), 122.3 (t, $^4J_{PC}$ = 1.2 Hz, m-Mes*), 109.2 (t, $^1J_{PC}$ = 8.4 Hz, C_{sp2}), 38.3 (s, o-CMe$_3$), 35.0 (s, p-CMe$_3$), 34.3 (t, $^5J_{PC}$ = 4.5 Hz, o-CMe$_3$), 31.6 (s, p-CMe$_3$), 13.4 (pt, ($^1J_{PC}$ + $^3J_{PC}$)/2 = 18.3 Hz, PMe); UV–Vis (hexanes) λ_{max} ($\varepsilon \times 10^3$) 320 (11.0), 368 (8.0), 590 (1.0); HRMS (ESI) Found: m/z 606.4474, Calc. for C$_{40}$H$_{64}$P$_2$, 606.4478.

4.3. Sulfurization of **3i**

Compound **3i** (180 mg, 0.26 mmol), prepared according to our previous report [9], was allowed to react with sulfur (0.95 mmol as S) in dichloromethane at room temperature for 12 h. The solvent was removed in vacuo and the residual materials were purified by silica gel column chromatography (chloroform) to afford **6** (89.9 mg, 47% yield).

Compound **6**: dark orange plates (hexane/CH$_2$Cl$_2$), mp 206–208 °C (decomp); ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ = 101.7 (d, $^2J_{PP}$ = 194.2 Hz, i-Pr$_2$NP), 45.7 (d, $^2J_{PP}$ = 194.2 Hz, MeP); ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.47 (2H, s, m-Mes*), 7.36 (2H, s, m-Mes*), 3.45 (2H, dsept, $^3J_{PH}$ = 13.4 Hz, $^3J_{HH}$ = 6.8 Hz, CH), 2.20 (3H, d, $^2J_{PH}$ = 11.9 Hz, PMe), 1.77 (18H, s, o-t-Bu), 1.61 (18H, s, o-t-Bu), 1.32 (18H, s, p-t-Bu), 1.21 (12H, d, $^3J_{HH}$ = 6.8 Hz, Me); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ = 155.7 (dd, $^2J_{PC}$ = 9.9 Hz, $^2J_{PC}$ = 4.8 Hz, $ipso$-Mes*), 153.0 (dd, $^3J_{PC}$ = 8.8 Hz, $^3J_{PC}$ = 3.7 Hz, o-Mes*), 147.6 (dd, $^3J_{PC}$ = 4.1 Hz, $^3J_{PC}$ = 2.6 Hz, o-Mes*), 124.7 (d, $^5J_{PC}$ = 2.2 Hz, p-Mes*), 124.6 (s, m-Mes*), 123.6 (s, m-Mes*), 55.6 (dd, $^1J_{PC}$ = 116.4 Hz, $^1J_{PC}$ = 53.7 Hz, P(=C)$_2$), 51.2 (s, CH), 40.0 (s, o-CMe$_3$), 39.1 (s, o-CMe$_3$), 36.5 (s, o-CMe$_3$), 35.0 (s, p-CMe$_3$), 34.9 (s, o-CMe$_3$), 31.7 (s, p-CMe$_3$), 29.1 (dd, $^1J_{PC}$ = 58.9 Hz, $^3J_{PC}$ = 19.2 Hz, PMe), 24.5 (d, $^3J_{PC}$ = 3.6 Hz, CHMe_2); EA Found: C, 72.26; H, 10.25, N, 1.81%, Calc. for C$_{45}$H$_{75}$NP$_2$S $\cdot$ 0.3CH$_2$Cl$_2$, C, 72.59; H, 10.17; N, 1.87%.

Compound **3i**: ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ = 150.7 (pt, ($^2J_{PC}$ + $^2J_{PC}$)/2 = 8.8 Hz, $ipso$-Mes*), 150.4 (d, $^3J_{PC}$ = 10.3 Hz, o-Mes*), 145.1 (s, p-Mes*), 133.3 (d, $^5J_{PC}$ = 4.6 Hz, o-Mes*), 123.3 (s, m-Mes*), 120.7 (s, m-Mes*), 103.2 (dd, $^1J_{PC}$ = 7.4 Hz, $^1J_{PC}$ = 1.0 Hz, C_{sp2}), 50.4 (d, $^2J_{PC}$ = 3.7 Hz, CH), 38.9 (s, o-CMe$_3$), 38.0 (s, o-CMe$_3$), 35.4 (d, $^5J_{PC}$ = 2.7 Hz, o-CMe$_3$), 35.0 (s, p-CMe$_3$),

34.0 (d, $^5J_{PC}$ = 8.4 Hz, o-CMe_3), 31.9 (s, p-CMe_3), 23.8 (s, CHMe_2), 14.2 (dd, $^1J_{PC}$ = 68.0 Hz, $^3J_{PC}$ = 28.0 Hz, PMe).

Acknowledgements

Appendix A. Supplementary data

CCDC 622119 and 622120 contains the supplementary crystallographic data for **3e** and **3h**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.10.066.

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