Phosphorus Heterocycles

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Access to Air-Stable 1,3-Diphosphacyclobutane-2,4-diyls by an Arylation Reaction with Arynes

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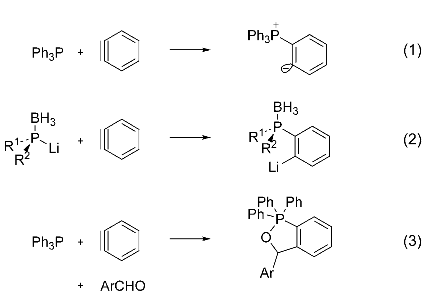
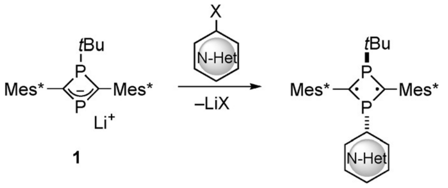
Abstract: *Tuning of the physicochemical properties of the 1,3-diphosphacyclobutane-2,4-diyl unit is attractive in view of materials applications. The use of arynes is shown to be effective for installing relatively electron rich aryl substituents into the open-shell singlet P-heterocyclic system. Treatment of the sterically encumbered 1,3-diphosphacyclobuten-4-yl anion with ortho-silylated aryl triflates in the presence of fluoride under appropriate conditions afforded the corresponding 1-aryl 1,3-diphosphacyclobutane-2,4-diyls. The air-stable open-shell singlet P-heterocycles exhibit considerable electron-donating character, and the aromatic substituent influences the open-shell character, which is thought to be related to the property of p-type semiconductivity. The P-arylated 1,3-diphosphacyclobutane-2,4-diyl systems can be further utilized as detectors of hydrogen fluoride (HF), which causes a remarkable change in their photoabsorption properties.*

Arynes are normally quite unstable and hard to isolate; however, various methods for the generation of arynes have been established and widely employed in organic synthesis.[1] Arynes have also played key roles in organophosphorus chemistry (Scheme 1). Wittig and co-workers reported the reaction of arynes (dehydroaromatic compounds), generated from fluoroarenes and butyllithium, with triarylphosphines to afford the corresponding zwitterionic betaines [Scheme 1, Eq. (1)].[2,3] This reaction procedure was utilized for the synthesis of a variety of organophosphorus compounds. Jugé and co-workers reported the synthesis of optically active phosphine–borane derivatives [Scheme 1, Eq. (2)].[4] Biju and co-workers used the addition of phosphines to arynes in a multicomponent [3+2] cycloaddition with aldehydes [Scheme 1, Eq. (3)].[5] Strongly electrophilic arynes accept even phosphines readily, and can provide functionalized phosphorus compounds with aryl substituents.



Scheme 1. Addition of phosphines to arynes.

We previously reported that nucleophilic aromatic substitution (S_NAr) of a sterically encumbered 1,3-diphosphacyclobuten-4-yl anion **1** can undergo arylation at the non-*tert*-butyl-substituted skeletal phosphorus atom to provide air-stable 1-aryl 1,3-diphosphacyclobutane-2,4-diyls (Scheme 2).



Scheme 2. S_NAr reaction of **1** with an electron-deficient N-heteroaryl reagent. Mes* = 2,4,6-$t\text{Bu}_3\text{C}_6\text{H}_2$.

The direct arylation is suitable for tuning the electronic properties of the open-shell singlet P-heterocyclic moiety, and is promising for the development of materials, such as organoelectronics,[6] and sensing/operating processes involving hydrogen fluoride (HF).[7] However, the S_NAr process was only successful when electron-deficient N-heterocyclic aryl halides were employed as the electrophiles, because the sp^2 phosphorus atom of **1** is positive in nature and scarcely contributes to the HOMO of **1**.[7] The development of novel methods for the direct arylation of 1,3-diphosphacyclobuten-4-yl anions with relatively electron rich aromatic substituents is quite attractive, as the experimentally characterized strong electron-donating nature of the resulting air-stable 1,3-diphosphacyclobutane-2,4-diyls makes these compounds suitable as p-type semiconductors and for the practical sensing of HF. Furthermore, installation of the electron-rich aromatic substituent on the phosphorus atom induces high stability owing to the enlarged HOMO–LUMO gap.

We speculated that highly electrophilic arynes should react with **1** and afford stable and electron-donating open-shell singlet P-heterocycles. Herein we demonstrate that arynes, generated from the corresponding *o*-silyl triflates and fluoride, react with **1** under appropriate conditions to provide air-stable open-shell singlet P-heterocycles **2**. The physicochemical properties of **2**, including their semiconductivity, were investigated. We also disclose the detection/release of hydrogen fluoride by the P-arylated 1,3-diphosphacyclobu-

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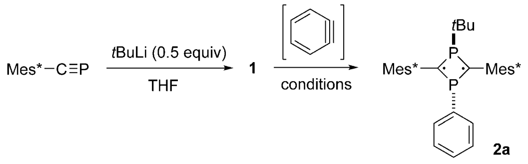
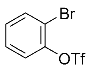
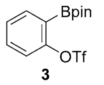
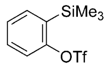
tane-2,4-diyls, with an accompanying remarkable change in their photoabsorption properties.

1-(2,4,6-Tri-*tert*-butylphenyl)-2-phosphaethyne was treated with *tert*-butyllithium (0.5 equiv) in THF to generate the corresponding cyclic anion **1**.[8] Next, conditions for the generation of benzyne were examined (Table 1). At first, a combination of *o*-bromophenyl triflate and an alkyl lithium[9] was used in THF at −78 °C, but the reaction gave an unidentified mixture (Table 1, entry 1). When the boronic acid derivative **3** was used as a precursor of benzyne and treated with *tert*-butyllithium,[10] the ^{31}P NMR spectrum of the reaction mixture showed the formation of **2a** as a single product; however, **2a** was isolated in very low yield owing to difficulties in its separation from the reaction mixture (Table 1, entry 2). To improve the yield of **2a**, we examined the reaction of the benzyne precursor 2-(trimethylsilyl)phenyl triflate (**4a**)[11] with **1** and TBAF at room temperature; however, the hydrofluorinated products of **2a** (see below), 1λ^5,3λ^5-diphosphetes,[7] were observed in the reaction mixture (Table 1, entry 3). On the other hand, the equivalent reaction at −20 °C afforded **3a** together with the hydrofluorinated products, thus indicating that the subsequent hydrofluorination was minimized at lower temperature (Table 1, entry 4). When the reaction was performed at −40 °C, the hydrofluorination was completely avoided, and the arylated product **2a** was isolated in 59 % yield (Table 1, entry 5).

Table 1: Arylation of **1** with benzyne.

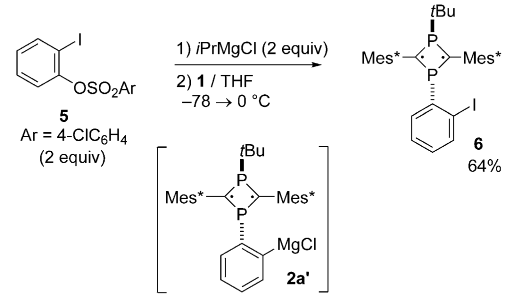


Entry	Conditions		Yield [%][a]
	generation of benzyne	arylation of **1**	
1	 *n*BuLi, −78 °C	−78 °C, 0.5 h	0
2	 **3** *t*BuLi, −78→−20 °C	RT, 2 h	14
3	 **4a** TBAF, 0 °C	0 °C→RT, 2.5 h	0[b]
4	**4a**, TBAF, −20 °C	−20 °C, 3 h	–[c]
5	**4a**, TBAF, −40 °C	−40 °C, 3 h	59

[a] Yield of **2a** (isolated product). [b] The hydrofluorinated product was observed. [c] Product **2a** and the hydrofluorinated product were observed in a ratio of 7:1. TBAF = tetrabutylammonium fluoride, pin = pinacolato, Tf = trifluoromethanesulfonyl.

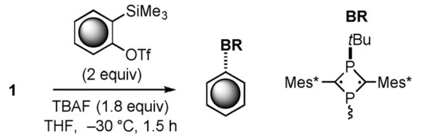
The addition of **1** to benzyne should generate the corresponding anionic intermediate, which would be protonated promptly. However, when *o*-iodoaryl sulfonate **5** was employed as a precursor of benzyne (Grignard reagent),[12] the 1,3-diphosphacyclobutane-2,4-diyl bearing a 2-iodophenyl substituent (**6**) was isolated in 64 % yield (Scheme 3), presumably via the anionic intermediate **2a′** and isopropyl iodide.

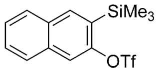
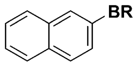
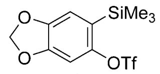
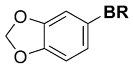
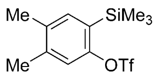
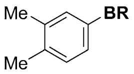
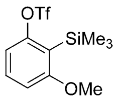
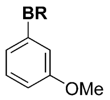
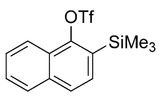
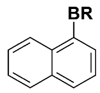
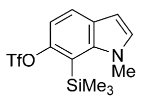
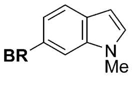
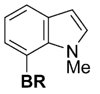
On the basis of the results summarized in Table 1, we examined the arylation of **1** with arynes to afford aryl-substituted 1,3-diphosphacyclobutane-2,4-diyls that were difficult to synthesize by the S$_N$Ar process (Table 2). A 2-naphthyl group was successfully installed by the use of **4b** as the precursor, and **2b** was isolated in 43 % yield (Table 2, entry 1). A benzo[*d*][1,3]dioxole moiety and 2,3-dimethyl-



Scheme 3. Reaction of **1** with benzyne generated with a Grignard reagent.

Table 2: Arylation of **1** with arynes.



Entry	Aryne precursor	Product(s)	Yield [%][a]
1	 **4b**	 **2b**	43
2	 **4c**	 **2c**	64
3	 **4d**	 **2d**	74
4	 **4e**	 **2e**	57
5	 **4f**	**2b** +  (9:1) **2f**	32[b]
6	 **4g**	 +  **2g** **2h** (7:1)	33[c]

[a] Yield of the isolated product. [b] The reaction was carried out at −40 °C for 3 h. [c] The reaction time was 2 h.

phenyl group were successfully combined with the open-shell P-heterocyclic unit, and **2c** and **2d** were isolated in moderate yields (Table 2, entries 2 and 3). Compound **2e** was selectively produced in 57 % yield (entry 4). This regioselectivity for **2e** could be explained by the inductive effect of the methoxy group to promote the observed *meta* selectivity.[13,14] No regioisomer of **2e** was observed in the reaction mixture. On the other hand, the naphthalene derivative **4f** gave a mixture of **2b** and **2f** with **2b** as the major product (Table 2, entry 5). Next, we examined reaction of **1** in the presence of **4g**, which normally reacts with predominant *meta* selectivity.[15] Although **2g** was obtained as the major product, a small amount of **2h** was also formed, presumably because of coordination of the nitrogen atom to the countercation (Li^+) of **1**.[16]

Table 3: Physicochemical properties of **2** and **6**.

Compound	λ_{max} [nm][a]	$E_{1/2}^{ox}$ (V vs. Ag/AgCl)[b]
2a	600	+0.29
2b	603	+0.30
2c	597	+0.28
2d	595	+0.26
2e	595	+0.30
6	559	+0.28

[a] In dichloromethane. [b] Conditions: 1 mM in dichloromethane, 0.1 M TBAP; working electrode: glassy carbon; counter electrode: Pt; scan rate: 50 mV sec^{-1}; ferrocene/ferrocenium: +0.54 V. TBAP = tetrabutylammonium perchlorate.

The physicochemical and structural properties of **2** and **6** were next investigated. The isolated products **2** all showed similar visible-absorption wavelengths (ca. 600 nm) and oxidation potentials (ca. +0.30 V; Table 3). As indicated previously,[6] the HOMO has a significant amplitude at the skeletal sp^2 carbon atoms and the Mes* aromatic rings. Nevertheless, the aryl substituent on the phosphorus atom affects the physicochemical properties.[6,7] The effect of the aromatic substituent on the 4-membered molecular system was almost identical for all compounds **2**. On the other hand, **6** showed a remarkable blueshift of photoabsorption as compared to **2a**, whereas the oxidation potential of **6** was almost identical to that of **2a**. The HOMO–LUMO energetic difference (4.91 eV) of **6**, optimized at the M06-2X/6-31G(d)/SDD level, was larger than that of **2a** (4.68 eV; M06-2X/6-31G(d)).

The molecular structure of **2b** was determined by X-ray crystallography and revealed comparable metric parameters to those of the previously reported air-stable 1,3-diphosphacyclobutane-2,4-diyls (see Figure S1 in the Supporting Information). DFT and CASSCF(6,6) calculations for **2b** identified remarkable contributions of the 2-naphthyl substituent to the molecular orbitals and the open-shell character. Figure 1 displays drawings of the orbitals HOMO−1 (#207) and LUMO+1 (#210), which show considerable contributions by the naphthyl substituent (see also Figure S2). As indicated by the estimated amount of electrons, the fused aromatic substituent is decisive in establishing the extremely stable open-shell character and thus p-type semiconductivity, although the mobility and on/off ratio of a drop-cast fabricated field-effect transistor (FET) were low ($\mu_h = 1.29 \times 10^{-8}$ cm^2 V^{-1} s^{-1}, On/Off = 6, $V_{th} = -4$ V; see the Supporting Information). Thus, the synthetic procedure based on the use of arynes would be beneficial for the development of stable congeners of cyclobutane-1,3-diyl that are significantly perturbed by (π-extended) aromatic substituents.

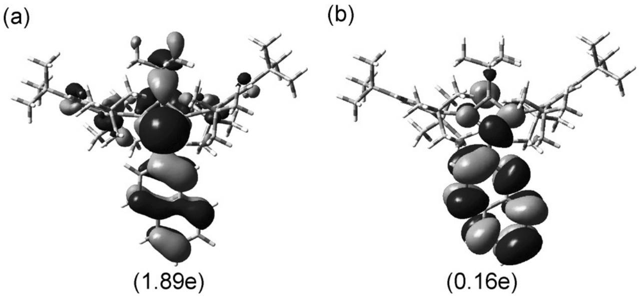
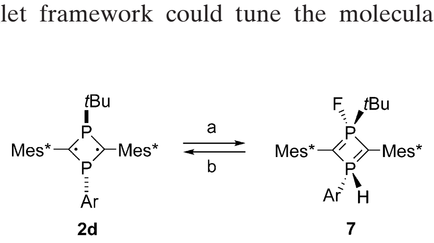


Figure 1. a) HOMO−1 (#207) and b) LUMO+1 (#210) of **2b** [M06-2X/6-31G(d)]. Values in parenthesis indicate the estimated amount of electrons [CASSCF(6,6)/6-31G(d)].

In an attempt to utilize **2** for a chemical transformation, we examined the detection of HF by **2**. In our previous study, 1,3-diphosphacyclobutane-2,4-diyls bearing relatively electron donating substituents trapped HF to afford 1λ^5,3λ^5-diphosphetes containing P−H and P−F bonds, and the trapped HF could be removed upon treatment with sodium hydride to recover the P-heterocyclic biradical system.[7] In our study of HF trapping by the open-shell P-heterocyclic system, the electron-rich 1,3-diphosphacyclobutane-2,4-diyl system showed a remarkable blueshift of photoabsorption assigned as the transition from the HOMO to the LUMO, which enabled the identification of the presence of HF by visual observation. Compound **2d** showed a weak visible absorption (595 nm) due to this HOMO–LUMO transition, whereas **7** (Scheme 4), with a higher-lying LUMO as compared to that of **2d**, showed remarkably different photoabsorption characteristics (Figure 2). Thus, **2d** can be used as a chemical probe for the detection of HF by the naked eye (see Figure S3).

In conclusion, arynes enabled the synthesis of P-arylated air-stable 1,3-diphosphacycyclobutane-2,4-diyls that were difficult to prepare by the previously established S$_N$Ar process. The installation of relatively electron rich and π-extended aryl substituents on a skeletal phosphorus atom of the open-shell singlet framework could tune the molecular orbitals



Scheme 4. Hydrofluorination of **2d** and removal of HF: a) C_5H_5N (2.0 equiv), Et_2NH (4.1 equiv), THF, room temperature, 24 h; b) NaH (2.0 equiv), 15-crown-5 (2.0 equiv), THF, room temperature, 20 h. Ar = 3,4-$Me_2C_6H_3$.

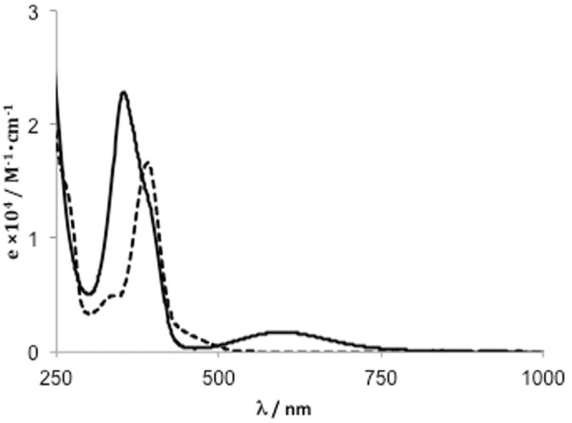


Figure 2. UV/Vis spectra of **2d** (solid line) and **7** (dashed line).

effectively for the development of highly electron donating molecular chromophores and the detection of hydrogen fluoride. To develop novel functional open-shell singlet molecules, we are attempting to synthesize P congeners of cyclobutane-1,3-diyls with π-extended and/or highly functionalized aromatic substituents by using various 1,3-diphosphacyclobuten-4-yl anions.

Experimental Section

2b: *tert*-Butyllithium (0.520 mmol) was added slowly to a solution of 2-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethyne (300 mg, 1.04 mmol) in THF (24 mL) at −78 °C under an argon atmosphere. The resulting mixture was stirred for 15 min and then allowed to warm to room temperature. The reaction mixture was cooled back down to −30 °C, and 3-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate (0.288 mL, 1.04 mmol) was added. TBAF (0.936 mmol) was then added dropwise, and the mixture was stirred for 1.5 h at −30 °C. Hexane and MeCN were added at this temperature, and the phases were separated. The hexane layer was washed three times with MeCN, and the solvent was removed in vacuo. The residual solid was washed with MeOH to afford **2b** (170 mg, 43 % yield) as a blue-green solid. M.p.: 129–132 °C (dec.); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.85$ (d, ^{3}J(P,H) = 14.1 Hz, 9 H, *t*BuP), 1.35 (s, 18 H, *p*-*t*Bu), 1.49 (s, 18 H, *o*-*t*Bu), 1.72 (s, 18 H, *o*-*t*Bu), 7.28–7.40 (m, 5 H), 7.46–7.67 (m, 4 H), 7.68–7.71 ppm (m, 2 H); ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): $\delta = -10.2$ (d, ^{2}J(P,P) = 347.5 Hz, ArP), 56.9 ppm (d, ^{2}J(P,P) = 347.5 Hz, *t*BuP); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 29.6$ (dd, ^{2}J(P,C), ^{4}J(P,C) = 3.8, 5.3 Hz, PC*Me*$_3$), 31.7 (s, *p*-C*Me*$_3$), 33.8 (d, ^{5}J(P,C) = 7.5 Hz, *o*-C*Me*$_3$), 34.8 (s, *p*-*C*Me$_3$), 35.3 (s, *o*-C*Me*$_3$), 38.0 (s, *o*-*C*Me$_3$), 38.9 (s, *o*-*C*Me$_3$), 47.6 (dd, ^{1}J(P,C) = 54.3 Hz, ^{3}J(P,C) = 13.6 Hz, P*C*Me$_3$), 104.8 (br s, CP$_2$), 121.1 (s, *m*-Mes*), 123.2 (s, *m*-Mes*), 126.3 (s, Nap), 126.3 (s, Nap), 126.7 (d, ^{3}J(P,C) = 5.3 Hz, *m*-Nap), 127.0 (d, ^{2}J(P,C) = 12.1 Hz, *o*-Nap), 127.7 (s, Nap), 128.0 (s, Nap), 129.5 (dd, ^{2}J(P,C) = 10.6 Hz, ^{2}J(P,C) = 3.8 Hz, *o*-Nap), 132.6–132.7 (m, 2C), 133.3 (s, *ipso*-Mes*), 134.3 (dd, ^{1}J(P,C) = 56.6 Hz, ^{3}J(P,C) = 24.2 Hz, *ipso*-Nap), 145.4 (s, *p*-Mes*), 148.5 (d, ^{3}J(P,C) = 9.8 Hz, *o*-Mes*), 150.5 ppm (pt, {^{3}J(P,C) + ^{3}J(P,C)}/2 = 8.3 Hz, *o*-Mes*); MS(ESI): *m*/*z* calcd for $C_{52}H_{74}P_2$ $[M]^{+\bullet}$: 760.5265; found: 760.5302.

7: NHEt$_2$ (253 μL, 2.46 mmol) was added to a solution of **2d** (443 mg, 0.60 mmol) and pentafluoropyridine (125 μL, 1.2 mmol) in THF (4 mL) at room temperature under an argon atmosphere. The mixture was stirred for 24 h at that temperature, and then the solvent was removed in vacuo, and the resulting residue was dissolved in hexane. The hexane solution was washed with MeCN, and the solvent was removed in vacuo. The residual solid was washed with EtOH to afford **7** (291 mg, 64 % yield) as a yellow solid: M.p.: 199–202 °C (dec.); ^{1}H NMR (300 MHz, [D$_8$]THF): $\delta = 0.41$ (d, ^{3}J(P,H) = 16.2 Hz, 9 H, *t*BuP), 1.22 (s, 18 H, *p*-*t*Bu), 1.46 (s, 18 H, *o*-*t*Bu), 1.53 (s, 18 H, *o*-*t*Bu), 2.29 (s, 3 H, Me), 2.32 (s, 3 H, Me), 7.03 (s, 2 H, *m*-Mes*), 7.21–7.26 (m, 3 H, *m*-Mes* + Ph), 7.80 (dd, *J* = 13.7 Hz, *J* = 7.7 Hz, 1 H, Ph), 7.91 (d, *J* = 13.5 Hz, 1 H, Ph), 8.28 ppm (ddd, ^{1}J(P,H) = 463.1 Hz, ^{4}J(F,H) = 52.2 Hz, ^{3}J(P,H) = 41.7 Hz, PH); ^{31}P{^{1}H} NMR (121 MHz, [D$_8$]THF): $\delta = 7.3$ (d, ^{2}J(P,P) = 131.2 Hz, ArP), 75.0 ppm (dd, ^{1}J(P,F) = 1106.9 Hz, ^{2}J(P,P) = 131.2 Hz, *t*BuP); ^{19}F NMR (282 MHz, [D$_8$]THF) $\delta = -64.1$ ppm (dd, ^{1}J(P,F) = 1107.0 Hz, ^{4}J(H,F) = 52.5 Hz); ^{13}C NMR (75 MHz, [D$_8$]THF): $\delta = 19.6$ (s, Me), 19.7 (s, Me), 26.5 (s, PC*Me*$_3$), 31.1 (ddd, ^{1}J(P,C) = 103.4 Hz, ^{1}J(P,C) = 92.1 Hz, ^{2}J(F,C) = 23.4 Hz, CP$_2$), 31.6 (s, *p*-C*Me*$_3$), 34.0 (d, ^{5}J(P,C) = 2.3 Hz, *o*-C*Me*$_3$), 34.6 (s, *p*-*C*Me$_3$), 35.0 (d, ^{5}J(P,C) = 3.0 Hz, *o*-C*Me*$_3$), 37.1 (s, *o*-*C*Me$_3$), 38.8 (ddd, ^{1}J(P,C) = 66.4 Hz, ^{2}J(F,C) = 31.7 Hz, ^{3}J(P,C) = 14.3 Hz, P*C*Me$_3$), 39.5 (s, *o*-*C*Me$_3$), 119.4 (s, *m*-Mes*), 124.5 (d, ^{4}J(P,C) = 3.0 Hz, *m*-Mes*), 128.1 (dd, ^{1}J(P,C) = 61.5 Hz, ^{3}J(P,C) = 7.2 Hz, *ipso*-Ph), 129.2 (d, ^{2}J(P,C) = 2.3 Hz, *ipso*-Mes*), 130.1 (d, ^{2}J(P,C) = 12.1 Hz, Ph), 132.9 (d, ^{3}J(P,C) = 12.1 Hz, Ph), 136.5 (d, ^{2}J(P,C) = 12.1 Hz, Ph), 137.2 (d, ^{3}J(P,C) = 12.1 Hz, Ph), 141.8 (d, ^{4}J(P,C) = 3.0 Hz, *p*-Ph), 143.9 (pt, {^{5}J(P,C) + ^{5}J(P,C)}/2 = 2.6 Hz, *p*-Mes*), 150.8 (d, ^{3}J(P,C) = 6.8 Hz, *o*-Mes*), 151.2 ppm (dd, ^{3}J(P,C) = 13.2 Hz, ^{3}J(P,C) = 8.7 Hz, *o*-Mes*); MS(APCI): *m*/*z* calcd for $C_{50}H_{77}F_1P_2$ $[M + H]^{+}$: 759.5586; found: 759.5563.

Removal of HF from **7**: 15-Crown-5 (19.8 μL, 0.10 mmol) was added to a solution of **7** (38 mg, 0.050 mmol) and 60 % NaH (4.0 mg, 0.10 mmol) in THF (1 mL) at room temperature under an argon atmosphere. The mixture was stirred for 20 h at that temperature, and then the solvent was removed in vacuo, and the resulting residue was dissolved in hexane. The hexane solution was washed with MeCN, and the solvent was removed in vacuo. The residual solid was washed with MeOH to afford **2a** (20.1 mg, 54 % yield) as a blue solid.

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