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Synthesis of Phosphorus Ylides Bearing a P−H Bond from a Kinetically Stabilized 1,3,6-Triphosphafulvene

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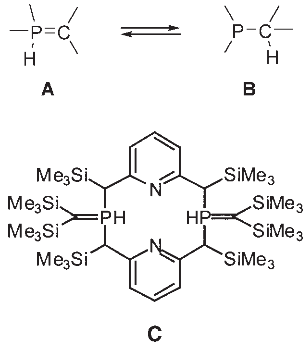
Abstract: In mixing 2,4,6-tris(2,4,6-tri-*tert*-butylphenyl)-1,3,6-triphosphafulvene with alkyllithium compounds and acetic acid, both of nucleophilic alkylation and electrophilic protonation occurred at the *exo* sp^2-phosphorus atoms to afford [2,4-bis(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphacyclopentadienylidene](alkyl)(2,4,6-tri-*tert*-butylphenyl)phosphoranes which are phosphorus ylides that bear a P−H bond. A phosphorus ylide bearing both P−H and P−F bonds was obtained by reaction of 2,4,6-tris(2,4,6-tri-*tert*-butylphenyl)-1,3,6-triphosphafulvene with hydrogen tetrafluoroborate, and the structure was determined by X-ray crystallography. Both P=C double bond and P$^+$−C$^-$ zwitterionic character was indicated by the metric parameters. The isolated phosphorus ylide bearing a P−H bond, [2,4-bis(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphacyclopentadienylidene](2,4,6-tri-*tert*-butylphenyl)phosphorane, showed no isomerization by H-migration to the corresponding phosphinodiphospholes, probably due to the π-accepting ability of the unsaturated PC bonds and aromaticity of the C_3P_2 ring. The ylide structure and aromaticity of 2,4-diphosphacyclopenta-2,4-dienylidenephosphorane was characterized by theoretical calculations. In addition, the regioselective protonation of the lithiated phosphinodiphospholes generated from the 1,3,6-triphosphafulvene is discussed.

Keywords: ab initio calculations · phosphaalkenes · phosphorus heterocycles · ylides · zwitterions

Introduction

Alkylidenephosphoranes [$R^1_3P{=}CR^2_2$], alternatively named phosphonium alkylides and usually called phosphorus ylides,[1] are one of the basic phosphorus compounds in organic chemistry since Wittig et al. started to develop the synthesis of olefins from carbonyl compounds.[1–5] Whereas a number of these phosphorus ylides have been synthesized and their properties have been studied, phosphorus ylides bearing a P−H bond (**A**) are rare, because they are unstable and easily isomerize to the corresponding phosphines (**B**) (Scheme 1).[5] The instability of **A** relative to **B** shows a sharp contrast to the case of phosphine oxides bearing a P−H bond [>P(=O)H], which predominate over phosphinous acids [>P−OH] because of the stability of the P=O bond. One approach for stabilizing structure **A** is to employ electron-withdrawing substituents such as ester groups, which causes delocalization of negative charge, together with kinetic stabilization by bulky substituents.[5] Indeed, Kolodiazhnyi reported the tautomeric equilibrium between $R_2P{-}CH(CO_2Me)_2$ and $R_2PH{=}C(CO_2Me)_2$, where R is a bulky alkyl group.[5,6] An alternative approach to synthesize phosphorus ylides with a P−H bond was demonstrated by Ber-



Scheme 1.

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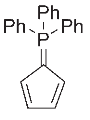
trand and co-workers who utilized bulky diisopropylamino groups and the P=C=P skeleton for the preparation of phosphorus ylides bearing P–H bonds ($(R_2N)_2PH{=}C{=}PX(NR_2)_2$; X = H or F, R = *i*Pr).[7] Recently, Niecke and co-workers have succeeded in isolating cyclic phosphorus ylide **C** where trimethylsilyl groups and pyridyl groups stabilize the >P(H)=C< system.[8]

One of the stable phosphorus ylides is (cyclopenta-2,4-dienylidene)triphenylphosphorane (the Ramirez ylide) **1** because the cyclopentadienyl ring displays aromaticity upon reduction.[9–11] Likewise, we have previously synthesized



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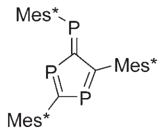
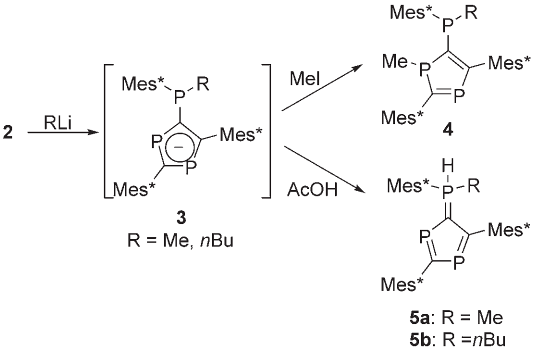


2

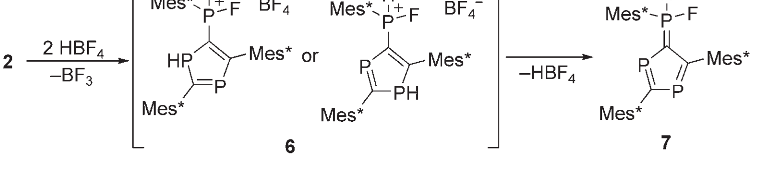
1,3,6-triphosphafulvene **2** from a formal trimerization of the phosphanylidene carbenoid [Mes*P=CBrLi] (Mes* = 2,4,6-tri-*tert*-butylphenyl).[12,13] Compound **2** contains the 1,3-diphosphacyclopentadiene skeleton which is a congener of cyclopentadiene. Taking the similarity between the P=C bonds and C=C bonds into consideration,[14] the C_3P_2 five-membered ring is expected to show a similar nature to cyclopentadienes. Furthermore, the P=C moiety shows good π-electron-accepting ability due to the low-lying LUMO, which effectively stabilizes the adjacent negative charge.[14–17] Therefore, we expected **2** to be a promising starting material for the synthesis of phosphorus ylides bearing a P–H bond, and herein we report our findings. The structures of the resulting phosphorus ylides bearing a P–H bond were determined by X-ray crystallography. Furthermore, we carried out theoretical studies on the structure and properties of cyclopenta-2,4-dienylidenephosphorane and the related compounds.

Results and Discussion

Preparation of phosphorus ylides with a P–H bond: As we demonstrated previously, regiospecific nucleophilic attack occurred at the 6-position of **2** to give the corresponding anion **3**, which affords the corresponding phosphinodiphospholes **4** upon quenching with iodomethane.[18] On the other hand, when acetic acid was employed as an electrophile for **3**, no phosphinodiphosphole was obtained, but rather the novel compounds **5** (Scheme 2). Spectroscopic data of **5** suggested a pentavalent phosphorane structure with a P–H group in the molecules. In the ^{31}P NMR spectrum of **5**, the peak at $\delta_P = -23.2$ (**5a**) or −4.5 ppm (**5b**) is accompanied by a considerably large *J*(P,H) coupling constant. These *J*(P,H) constants are close to the corresponding data of the reported phosphorus ylides with P–H bonds.[6–8] In the ^{13}C NMR spectrum of **5a**, one of the sp^2-carbon atoms in the C_3P_2 ring that connects with the phosphorane moiety was observed at relatively higher field ($\delta_C = 119.8$ ppm) than the other two carbon atoms ($\delta_C = 182.6$ and 171.4 ppm). In the ^{1}H NMR spectrum of **5**, the P-H proton was observed at $\delta_H = 7.64$ (**5a**) and 7.24 ppm (**5b**) accompanied by a large *J*(P,H) coupling constant. Compounds **5** neither decompose in air and even on silica gel nor isomerize to phosphinodiphospholes similar to **4**, suggesting that the 2,4-diphosphacyclopenta-2,4-dienyl group plays an important role in stabilizing the P–H ylide structures.



Scheme 2.



Scheme 3.

We have established an alternative procedure to prepare a stable ylide bearing a P–H bond from **2**. Compound **2** was allowed to react with hydrogen tetrafluoroborate in dichloromethane to generate a phosphonium salt **6** which was observed by ^{31}P NMR spectroscopy (Scheme 3). The solution of **6** was concentrated and phosphorus ylide **7** was generated upon addition of ethyl acetate. Finally **7** was purified by column chromatography on silica gel. The presence of P–H and P–F bonds in **7** was identified by ^{31}P and ^{1}H NMR spectroscopy, and three sp^2-carbon atoms in the C_3P_2 five-membered ring were observed by ^{13}C NMR spectroscopy. Similar to **5**, **7** showed no isomerization to phosphinodiphosphole derivatives. The synthetic procedures for **5** and **7** are regarded as an oxidative addition of R–H (R = Me, *n*Bu, F) at the *exo* sp^2-phosphorus atom of **2**, which resembles the reported procedure for preparation of a phosphorus ylide from phosphaalkene ($MesP{=}CPh_2$; Mes = 2,4,6-$Me_3C_6H_2$).[19] As for the regioselective protonation of **3**, we have carried out theoretical calculations. Attempts to clarify the formation mechanism of **5** and **7** are in progress.

Molecular structure: Single crystals of **7** were obtained and analyzed by X-ray crystallography. Figure 1 displays an

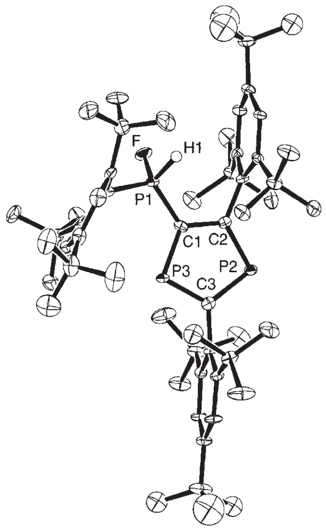
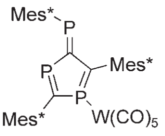
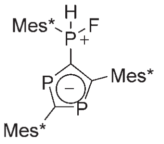


Figure 1. Structure of **7** (ORTEP drawing; 50% probability ellipsoids). Hydrogen atoms except for H1 are omitted for clarity. The two *p-tert*-butyl groups in the Mes* groups at C2 and C3 are disordered, and the atoms with predominant occupancy factors (0.60 and 0.60, respectively) are displayed. Selected bond lengths [Å] and angles [°]: P1–F 1.560(4), P1–C1 1.708(7), P1–C_{Mes^*} 1.784(7), P2–C2 1.736(7), P2–C3 1.769(7), P3–C1 1.778(6), P3–C3 1.724(7), C1–C2 1.454(7), C2–C_{Mes^*} 1.505(7), C3–C_{Mes^*} 1.526(8), P1–H1 1.347; C1-P1-F 112.8(3), F-P1-C_{Mes^*} 113.7(3), C1-P1-C_{Mes^*} 114.3(3), C2-P2-C3 97.3(3), C1-P3-C3 96.0(3), P1-C1-P3 123.4(3), P1-C1-P2 119.9(4), P3-C1-C2 116.1(5), P2-C2-P1 114.6(4), P2-C2-C_{Mes^*} 128.6(4), P1-C2-C_{Mes^*} 128.6(4), P2-C3-P3 115.9(4).

ORTEP drawing of the structure of **7** together with selected metric parameters. The five-membered C_3P_2 ring and the P1 atom are coplanar (Θ(P1-C1-P3-C3) 174.9(4)°, Θ(P1-C1-C2-P2) 175.4(4)°, Θ(P2-C2-C1-P3) 3.9(6)°, Θ(P2-C3-P3-C1) 2.3(4)°, Θ(P3-C3-P2-C2) 0.5(4)°). The P1–C1 distance is close to that of the *exo* P=C bond of **2w** (1.710(6) Å)[12] and the corresponding bond in the Ramirez ylide **1** (1.718(2) Å).[11] On the other hand, the P2–C2 and P3–C3 bonds are longer than the corresponding bonds of **2w** (1.689(7), 1.703(7) Å), which is compensated for by contraction of the P2–C3 and P3–C1 bonds (P–C bonds in the C_3P_2 ring of **2w**: 1.815(6), 1.801(7) Å).[12] The C1–C2 bond is slightly longer than the corresponding bond of **2w** (1.447(8) Å),[12] probably due to repulsion between the Mes* group at the C2 atom and the *exo* phosphorane moiety. These metric parameters of **7** indicate the properties of phosphorus ylides that show both the characteristics of the "ylene" structure **7** and the zwitterionic structure **7A**.

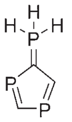


2w



7A

Theoretical calculations: To understand the structure and properties of **7** in detail, we performed theoretical calculations for 2,4-diphosphacyclopenta-2,4-dienylidenephosphorane (**8**) and the related compounds **9** and **10**. Calculations were performed with the Gaussian03 quantum chemical program package.[20] Geometry optimizations and harmonic vibrational frequency calculations were carried out with the B3LYP functional and the cc-pVTZ basis set. Single point CCSD(T)/aug-cc-pVDZ calculations were performed on the geometries obtained with the B3LYP functional. Figure 2 displays optimized structures of **8**–**10** together with bond order data and atomic charges (the Wiberg indices). The structure of **8** is close to the observed structure of the C_3P_2 ring of **7** (Figure 1). The *exo* PC bond length of **8** is close to that of **9**, suggesting a P=C double bond. In agreement with this, recent theoretical investigations pointed out that the PC bond in methylenephosphorane [H_3PCH_2] displays the characteristics of a λ^5-P=C double bond.[21] On the other hand, the structure of the five-membered ring moiety of **8** is close to that of **10**. Accordingly, the observed structure of the C_3P_2 five-membered ring of **7** is similar to that of **10**. Furthermore, the atomic charge on the ylide carbon atom of **8** (−0.87) is more negative than those of the corresponding carbon atoms of **9** (−0.74) and **10** (−0.74). These properties of **7** and **8** suggest phosphorus ylides, which are often described by two canonical structures: ylenes [$R_3P{=}CR'_2$] and ylides [$R_3P^+{-}C^-R'_2$].



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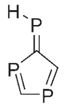

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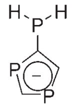

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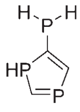

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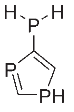

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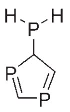

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Compounds **5** and **7** showed no isomerization through H-migration to the corresponding phosphinodiphospholes. However, **8** showed inferior stability compared with phosphinodiphospholes **11**–**13** according to calculations (Table 1). To study the regioselective protonation of **3**, we calculated the molecular electrostatic potential (MEP, visualized with the gOpenMol program[22]) maps of the anion **10** and its lithium complex (Figure 3). According to these results, in the case of the pure anion **10** (Figure 3a), the protonation is favored mainly on the ring, while in the lithium complex (Figure 3b) the *exo*-phosphorus atom is the main protonation side, which clearly shows the role of the kinetic effects in the formation of **5**.[8] Thus, the lithium atom plays an important role in the reactivity of **3**. On the other hand, in the reaction of **3** with iodomethane,[18] iodine might affect the regioselectivity, leading to **4**.

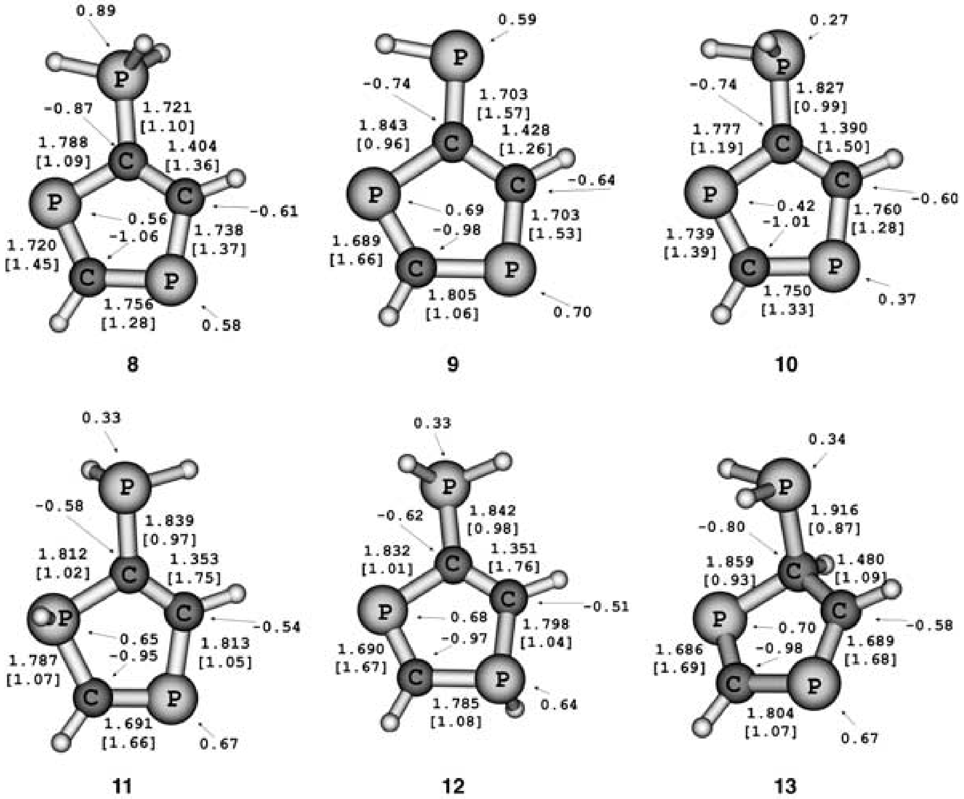

Figure 2. Bond lengths [Å] and Wiberg indices (in a.u. indicated in square brackets) and natural atomic charges (in a.u.) of **8**–**13**.

Table 1. Total and relative energies, and NICS indices for **8**–**13**.[a]

	E [a.u.]		E_{rel} [kJ mol^{-1}]		NICS [a.u.]
	B3LYP	CCSD(T)	B3LYP	CCSD(T)	B3LYP
8	−1141.45067	−1139.55030	52.93	62.70	−10.7
9	−1140.25143	–	–	–	0.5
10	−1140.94915	–	–	–	−10.9
11	−1141.47083	−1139.57418	0.00	0.00	−4.5
12	−1141.47045	−1139.57359	0.98	1.54	−5.1
13	−1141.46985	−1139.58113	2.58	−18.26	–

[a] Level of calculations: CCSD(T)/cc-pVTZ//B3LYP/cc-pVTZ.

Although λ^5-phosphorus ylides are normally less stable than the corresponding λ^3-phosphines, phosphorus ylides can be isolated due to the large activation energy for the isomerization.[23] In the case of phosphorus ylides bearing a P–H bond, the activation energy is small and thus they should be easily isomerized.[24] The stability of **5** and **7** might be attributed to the π-accepting effect of the P=C moiety[16,17,25] which prevents H-migration.[8] Additionally, the NICS value of **8** (−10.7 a.u.) is similar to that of **10** (−10.9 a.u.), which suggests that aromaticity[26] contributes to stabilize the ylide structure of **5** and **7**.[27] Conversely, **9** showed lower aromaticity (NICS = +0.5) compared with **8** (Table 1).

Conclusion

We have demonstrated that 1,3,6-triphosphafulvene **2** is a promising material for the preparation of phosphorus ylides bearing a P–H bond, and have synthesized **5** and **7**. We succeeded in determining the molecular structure of **7** which displays characteristics of phosphorus ylides, namely the P=C double bond structure and the polar zwitterionic structure. Theoretical calculations for **8** supported the ylide structures for the experimentally synthesized **5** and **7**. The π-electron-accepting effect of the 1,3-diphosphacyclopentadiene moiety seems to be quite effective in stabilizing the structures of **5** and **7**. The findings we have described herein will open new research areas in the chemistry of phosphorus ylides.

Experimental Section

5a: Compound **2** was prepared according to our previous report.[11,17] Methyllithium (0.064 mmol, 1.0 M solution in diethyl ether) was added to a solution of **2** (50 mg, 0.058 mmol) in THF (1 mL) at −78 °C, and acetic acid (0.35 mmol) was immediately added. The reaction mixture was allowed to warm up to room temperature and the solvent was removed in vacuo. Purification of the crude products by chromatography on silica gel (hexane/EtOAc 10:1) afforded **5a** (21 mg; 41 % yield). Yellow prisms (hexane), m.p. 185–187 °C; ^{31}P NMR (162 MHz, CDCl$_3$): $\delta = 233.7$ (d, J(P,P) = 28.3 Hz), 229.3 (ddd, J(P,P) = 97.2 Hz, J(P,P) = 28.3 Hz, J(P,H) = 5.8 Hz), −23.2 ppm (ddq, J(P,H) = 467.6 Hz, J(P,P) = 97.2 Hz, J(P,H) = 12.8 Hz); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.64$ (ddq, J(P,H) = 467.6 Hz, J(P,H) = 5.8 Hz, J(H,H) = 5.6 Hz, 1 H; PH) 7.53–7.38 (m, 6 H; arom), 2.26 (dd, J(P,H) = 12.8 Hz, J(H,H) = 5.6 Hz, 3 H; Me), 1.66 (s, 9 H; *t*Bu), 1.49 (s, 9 H; *t*Bu), 1.41 (s, 9 H; *t*Bu), 1.38 (s, 9 H; *t*Bu), 1.36 (s, 9 H; *t*Bu), 1.34 (s, 9 H; *t*Bu), 1.32 (s, 9 H; *t*Bu), 1.21 (s, 9 H; *t*Bu), 0.91 ppm (s, 9 H; *t*Bu); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): $\delta = 182.6$ (m; C2), 171.4 (d, J(P,C) = 46.7 Hz; C4), 159.1 (d, J(P,C) = 7.3 Hz; *o*-Mes*), 158.4 (d, J(P,C) = 8.8 Hz; *o*-Mes*), 154.5 (d, J(P,C) = 3.5 Hz; *p*-Mes*), 150.7 (d, J(P,C) = 6.0 Hz; *o*-Mes*), 149.3 (m; *o*-Mes*), 148.6 (s; *p*-Mes*), 146.4 (s; *p*-Mes*), 139.5 (pt, (J(P,C) + J(P,C))/2 = 22.0 Hz; *ipso*-Mes*), 135.5 (dd, J(P,C) = 24.3 Hz, J(P,C) = 9.9 Hz; *ipso*-Mes*), 127.6 (d, J(P,C) = 12.3 Hz; *m*-Mes*), 125.3 (d, J(P,C) = 12.2 Hz; *m*-Mes*), 123.9 (d, J(P,C) = 7.6 Hz; *m*-Mes*), 122.5 (d, J(P,C) = 8.3 Hz; *m*-Mes*), 119.8 (pt, (J(P,C) + J(P,C))/2 = 58.6 Hz; C5), 117.1 (d, J(P,C) = 74.8 Hz; *ipso*-Mes*), 39.5 (s; *o*-CMe$_3$), 39.2 (s; *o*-CMe$_3$), 39.1 (s; *o*-CMe$_3$), 38.9 (s; *o*-CMe$_3$), 35.5–34.3 (br.s; *o*-C*Me*$_3$, *p*-CMe$_3$), 31.7 (s; *p*-C*Me*$_3$), 31.6 (s; *p*-C*Me*$_3$), 31.1 (s; *p*-C*Me*$_3$), 20.6 ppm (dd, J(P,C) = 55.7 Hz, J(P,C) = 6.2 Hz; Me); UV (hexanes): $\lambda_{\max}(\log\varepsilon) = 356$ (3.72) nm; elemental analysis calcd (%) for $C_{58}H_{91}P_3\cdot H_2O$: C 77.46, H 10.42; found: C 77.69, H 10.59.

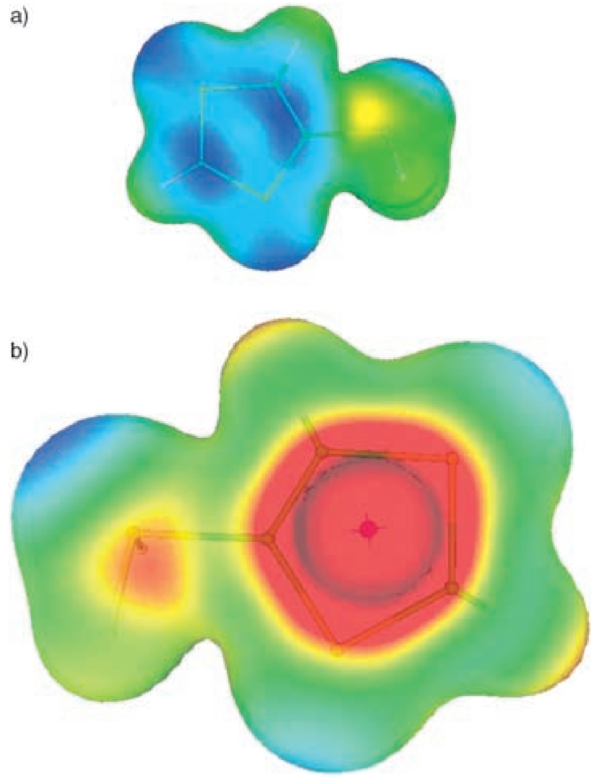

Figure 3. Molecular electrostatic potential mapped on the $\rho(\boldsymbol{r})=0.01$ a.u. electron density isosurface of anion **10** (a) and its lithium complex (b). Blue regions show the most negative (most nucleophilic) area of the molecule, while red regions indicate the less nucleophilic regions.

5b: Compound **2** (50 mg, 0.058 mmol) was allowed to react with butyllithium (0.064 mmol, 1.6 M solution in hexane) and acetic acid (0.35 mmol) to afford **5b** (23 mg, 44 % yield) after workup similar to that used in the synthesis of **5a**. Yellow prisms (hexane), m.p. 203–205 °C; ^{31}P NMR (162 MHz, CDCl$_3$): $\delta=240.0$ (ddm, J(P,P) = 113.2 Hz, J(P,P) = 27.3 Hz), 235.6 (d, J(P,P) = 27.3 Hz), −4.5 ppm (ddm, J(P,H) = 451.2 Hz, J(P,P) = 113.2 Hz); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=7.24$ (dm, J(P,H) = 451.2 Hz, 1H; PH), 7.58–7.50 (m, 6H; arom), 1.58 (s, 9H; *t*Bu), 1.54 (s, 9H; *t*Bu), 1.50 (s, 9H; *t*Bu), 1.48 (s, 9H; *t*Bu), 1.47 (s, 9H; *t*Bu), 1.38 (s, 9H; *t*Bu), 1.37 (s, 9H; *t*Bu), 1.35 (s, 9H; *t*Bu), 1.31 (s, 9H; *t*Bu), 0.54 ppm (t, J(H,H) = 7.0 Hz, 3H; Me) (the methylene protons of the butyl group were not assigned due to overlap with peaks of the *tert*-butyl groups); UV (hexanes): $\lambda_{max}(\log\varepsilon)=352$ (3.68) nm; elemental analysis calcd (%) for $C_{61}H_{97}P_3\cdot H_2O$: C 77.83, H 10.60; found: C 77.88, H 10.67.

7: Hydrogen tetrafluoroborate–diethyl ether complex (ca. 0.07 mmol) was added to a solution of **2** (20 mg, 0.023 mmol) in dichloromethane (1 mL) at room temperature. The reaction mixture was monitored by ^{31}P NMR spectroscopy to observe phosphonium salt **6** ($\delta_P=313.5$ (m), 42.5 (ddd, J(P,P) = 65.6 Hz, J(P,F) = 1116.0 Hz, J(P,H) = 601.2 Hz), 35.4 (dd, J(P,P) = 65.6 Hz, J(P,H) = 250.3 Hz)). The reaction mixture was concentrated in vacuo and the residue was dissolved in ethyl acetate (1 mL). The solution was concentrated and the residual materials were purified by column chromatography on silica gel (hexane/EtOAc 1:1) to afford **7** (7 mg; 32 % yield). Yellow prisms (hexane), m.p. 213–215 °C; ^{31}P NMR (162 MHz, CDCl$_3$): $\delta=249.4$ (dpt, J(P,P) = 34.5 Hz, (J(P,P) + J(P,F))/2 = 9.6 Hz), 247.0 (ddd, J(P,P) = 101.6 Hz, J(P,P) = 34.5 Hz, J(P,H) = 9.2 Hz), 45.2 ppm (dddd, J(P,F) = 1077.3 Hz, J(P,H) = 573.6 Hz, J(P,P) = 101.6 Hz, J(P,P) = 9.6 Hz); ^{1}H NMR (600 MHz, CDCl$_3$): $\delta=7.79$ (ddd, J(P,H) = 573.6 Hz, J(F,H) = 74.4 Hz, J(P,H) = 9.2 Hz, 1H; PH), 7.57 (s, 1H; arom), 7.55 (s, 1H; arom), 7.50 (s, 2H; arom), 7.47 (s, 2H; arom), 1.46 (s, 9H; *t*Bu), 1.43 (s, 18H; *t*Bu), 1.40 (s, 9H; *t*Bu), 1.37 (s, 9H; *t*Bu), 1.33 (s, 9H; *t*Bu), 1.28 (s, 18H; *t*Bu), 1.06 ppm (s, 9H; *t*Bu); ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$): $\delta=184.4$ (m; C2), 171.9 (d, J(P,C) = 46.5 Hz; C4), 157.5 (s; *p*-Mes*), 150.5 (d, J(P,C) = 4.5 Hz; *o*-Mes*), 148.9 (m; *o*-Mes*), 148.4 (m; *o*-Mes*), 147.9 (s; *p*-Mes*), 147.8 (d, J(P,C) = 4 Hz; *o*-Mes*), 146.0 (s; *p*-Mes*), 138.2 (pt, (J(P,C) + J(P,C))/2 = 20.2 Hz; *ipso*-Mes*), 135.9 (dd, J(P,C) = 20.5 Hz, J(P,C) = 10.5 Hz; *ipso*-Mes*), 122.4 (s; *m*-Mes*), 122.0 (s; *m*-Mes*), 122.0 (s; *m*-Mes*), 121.6 (s; *m*-Mes*), 118.6 (m; C5), 112.2 (dd, J(P,C) = 114.0 Hz, J(F,C) = 24.0 Hz; *ipso*-Mes*), 38.8 (s; *o*-CMe$_3$), 38.6 (s; *o*-CMe$_3$), 38.4 (s; *o*-CMe$_3$), 38.3 (s; *o*-CMe$_3$), 35.4 (s; *o*-C*Me*$_3$), 35.2 (s; *p*-CMe$_3$), 34.9 (s; *p*-CMe$_3$), 34.8 (s; *p*-CMe$_3$), 33.7 (s; *o*-C*Me*$_3$), 33.0 (s; *o*-C*Me*$_3$), 31.5 (s; *p*-C*Me*$_3$), 31.5 (s; *p*-C*Me*$_3$), 30.8 ppm (s; *p*-C*Me*$_3$); ^{19}F NMR (559 MHz, CDCl$_3$): $\delta=-93.7$ ppm (ddd, J(P,F) = 1077.3 Hz, J(F,H) = 74.4 Hz, J(P,F) = 9.6 Hz); UV (hexanes): $\lambda_{max}(\varepsilon)=381$ (3.79), 320 (3.96) nm; elemental analysis calcd (%) for $C_{57}H_{88}FP_3$: C 77.34, H 10.02; found: C 76.85, H 10.20.

X-ray crystallography for 7: A Rigaku RAXIS-IV imaging plate detector with graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda=0.71070$ Å) was used. The structure was solved by direct methods (SIR92),[28] expanded by using Fourier techniques (DIRDIF94),[29] and then refined by full-matrix least squares. Structure solution, refinement, and graphical representation were carried out using the teXsan package.[30] $C_{57}H_{88}FP_3$, $M_r=885.24$, crystal dimensions $0.20\times0.15\times0.10$ mm^3, triclinic, $P\bar{1}$ (no. 2), $a=11.3053(6)$, $b=23.251(2)$, $c=10.5962(9)$ Å, $\alpha=96.852(5)$, $\beta=95.130(4)$, $\gamma=91.659(2)°$, $V=2752.1(3)$ Å^3, $Z=2$, $T=133$ K, $2\theta_{max}=55.0°$, $\rho_{calcd}=1.068$ g cm^{-3}, $\mu(\mathrm{Mo}_{K\alpha})=0.145$ mm^{-1}, 22465 observed reflections, 11547 unique reflections ($R_{int}=0.068$), $R1=0.089$ ($I > 3\sigma(I)$), $R_W=0.198$ (all data), $S=1.41$ (544 parameters). CCDC-267116 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data request/cif.

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