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Note

Serendipitous Discovery of a Phosphirene−Phosphindole Rearrangement

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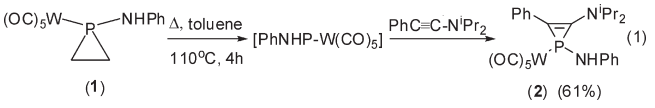
Summary: The reaction of strong Lewis acids with 2-amino-3-phenylphosphirene pentacarbonyltungsten complexes leads to the corresponding 2-aminophosphindoles through the unexpected formation of a bond between phosphorus and one of the ortho carbons of the phenyl ring.

The phosphirenylium cation has been characterized for the first time by Regitz in 1994[1] as a free species and in 1999 as a P−W(CO)$_5$ complex.[2] In spite of its 2 π aromaticity,[3] this cation appears to be quite difficult to make and must be kept in liquid SO_2 at low temperature. Wanting to stabilize this type of species for further studies, we noticed that an isoelectronic cyclopropenylidene had been successfully stabilized using amino substituents.[4] Following our work on 2-aminophosphirenes,[5] we decided to investigate the potential conversion of 1,2-diaminophosphirenes into 2-aminophosphirenylium cations. This research led us to the discovery of a completely unexpected rearrangement of 2-amino-3-phenylphosphirenes into 2-aminophosphindoles through the formation of a bond between phosphorus and one of the *ortho* carbons of the phenyl ring.

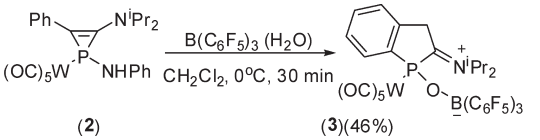
Results and Discussion

As usual for this kind of strained phosphorus−carbon heterocycles, we decided to work in the coordination sphere of tungsten for convenience. The products are easier to synthesize and more stable. The reaction of [PhNHP-W(CO)$_5$] as generated from the appropriate phosphirane precursor (**1**)[6] with PhC≡C−N^{i}Pr$_2$[7] affords the expected 1,2-diaminophosphirene (**2**) in good yield (eq 1).



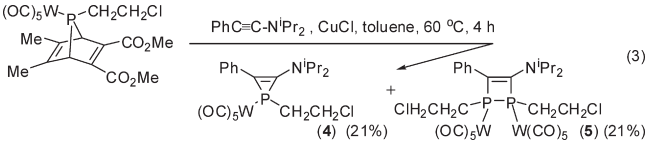
(1) (2) (61%) (1)

Phosphirene **2** shows the expected high-field shift of the ^{31}P resonance at ca. −100 ppm. Our initial attempt to convert **2** into the corresponding phosphirenylium by abstraction of the amino substituent at phosphorus using commercial tris(pentafluorophenyl)borane led to a completely unexpected ring expansion (eq 2).



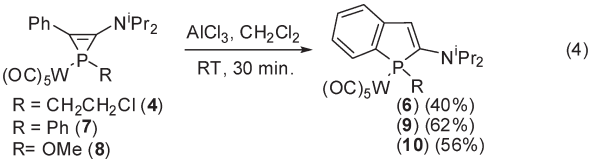
(2) (3)(46%) (2)

The structure of the 2-aminophosphindole (**3**) was established by X-ray crystal structure analysis (Figure 1). In fact, it is known that commercial tris(pentafluorophenyl)borane contains water and behaves as a strong protic acid.[8] It is clear that the first step of the reaction is a protonation of the nitrogen substituent at phosphorus, leading to a replacement of the P−N by the P−O bond. But the unexpected and puzzling finding is that another reaction takes place converting the phosphirene into the phosphindole ring. In order to avoid the perturbing effect of water, we decided to use another approach to phosphirenylium ions relying on the $AlCl_3$-induced dealkylation of 1-β-chloroethylphosphirenes.[2,9] The necessary phosphirene **4** was prepared as shown in eq 3.



(3)

The reaction of $AlCl_3$ with **4** at room temperature leads to the immediate formation of the corresponding phosphindole **6**. No phosphirenylium ion is observed, and the β-chloroethyl substituent at phosphorus remains intact. The identification of **6** was essentially carried out by NMR spectroscopy. Particularly significant are the single ethylenic proton at 5.86 ppm (J_{HP} = 22.5 Hz) and the CH_2Cl carbon at 39.0 ppm (J_{CP} = 6.6 Hz) in $CDCl_3$. We also used the already described aminophosphirenes **7** and **8**[5] to demonstrate the generality of this ring expansion (eq 4).



(4)

The phosphindole **9** was characterized by X-ray crystal structure analysis (Figure 2). To the best of our knowledge,

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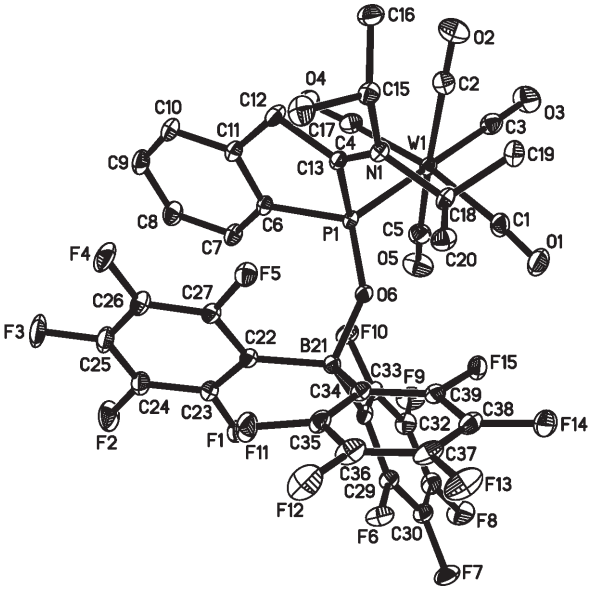


Figure 1. X-ray crystal structure analysis of phosphindole **3**. Significant distances (Å) and angles (deg): P1−W1 2.4885(6), P1−O6 1.5599(16), P1−C6 1.815(2), P1−C13 1.895(2), C13−N1 1.292(3), C13−C12 1.502(3), C12−C11 1.507(3), C6−C11 1.398(3), O6−B21 1.540(3); C6−P1−C13 89.53(9), C6−P1−O6113. 19(9), C13−P1−O6 108.26(9), P1−C13−N1 127.68(16), C12−C13−N1 122.82(19).

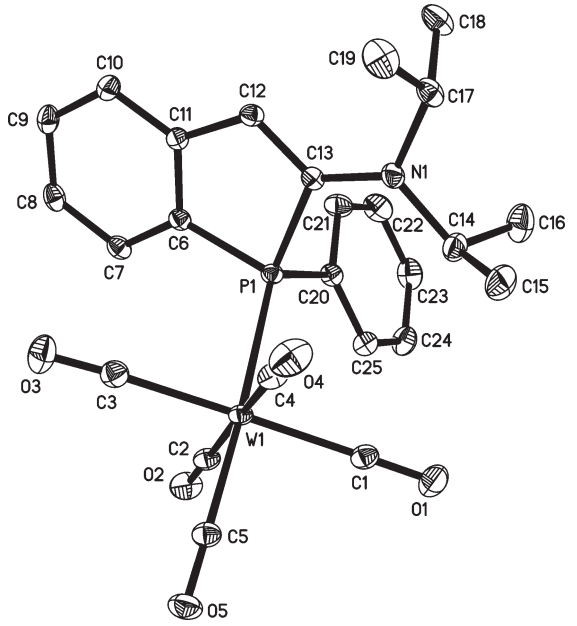


Figure 2. X-ray crystal structure analysis of phosphindole **9**. Significant distances (Å) and angles (deg): P1−W1 2.5307(3), P1−C6 1.8032(13), P1−C13 1.8503(13), C12−C13 1.3672(17), C11−C12 1.4459(18), C6−C11 1.4019(18), C13−N1 1.3640(16); C6−P1−C13 91.34(6), C13−N1−C14 120.36(12), C13−N1−C17 121.90(11), C14−N1−C17 116.35(11).

2-aminophosphindoles were unknown until now, and thus, this easy transformation already has a synthetic interest. However, we were also puzzled by the fact that the *ortho* carbon of the phenyl substituent at C_2 that becomes bonded to phosphorus is geometrically far away from this heteroatom. A drastic distortion of the molecule is thus needed to create this bond. In order to shed some light on this unprecedented rearrangement, we decided to study by DFT calculations the interaction between the aminophosphirene complex **11** and BH_3, chosen as the simplest representative Lewis acid. We suspected that BH_3 might coordinate to the carbon bearing the phenyl substituent. The calculations were carried out at the B3LYP/6-31G(d)-lanl2dz (W) level. They indeed confirmed that a well-defined adduct (**11**BH_3) is formed (no negative frequency). Its structure is shown in Figure 3.

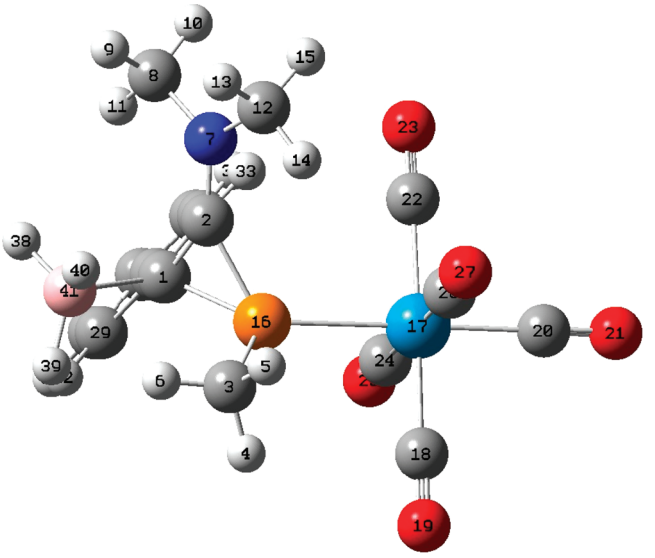
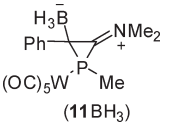
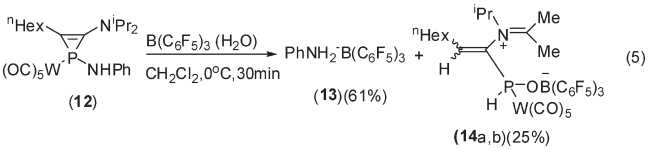


Figure 3. Computed structure of **11**BH_3 at the B3LYP/6-31+G(d)-lanl2dz(W) level. Significant distances (Å) and angles (deg): P16−C1 1.911, P16−C2 1.804, C1−C2 1.410, C1−B41 1.755, C2−N7 1.306; C1−P16−C2 44.48, P16−C1−C28 123.61, P16−C1−B41 111.77.



The B−C interaction is weak (1.755 vs 1.59 Å for the sum of the covalent radii) but sufficient to induce a sizable weakening of the corresponding P−C phosphirene bond, which is elongated from ca. 1.768 in the free species (X-ray)[5] to 1.911 Å in **11**C, and the development of a strong positive charge at phosphorus (Mulliken charge +0.63). On this basis, we suggest that the mechanism of the ring expansion involves the breaking of the P−C(Ph) phosphirene bond induced by the Lewis acid, followed by the electrophilic attack of P onto the *ortho* carbon of the phenyl ring.

What happens when no phenyl substituent is present on the phosphirene ring? Under strictly identical conditions as for **2**, the diaminophosphirene **12** reacts with the borane to give the borane-aniline adduct **13** and a mixture of two isomeric open-chain secondary phosphines (**14**a,b) (eq 5).



The formula of **13** was established by X-ray crystal structure analysis. The two isomers of **14** (δ^{31}P(**14**a) 68.8,

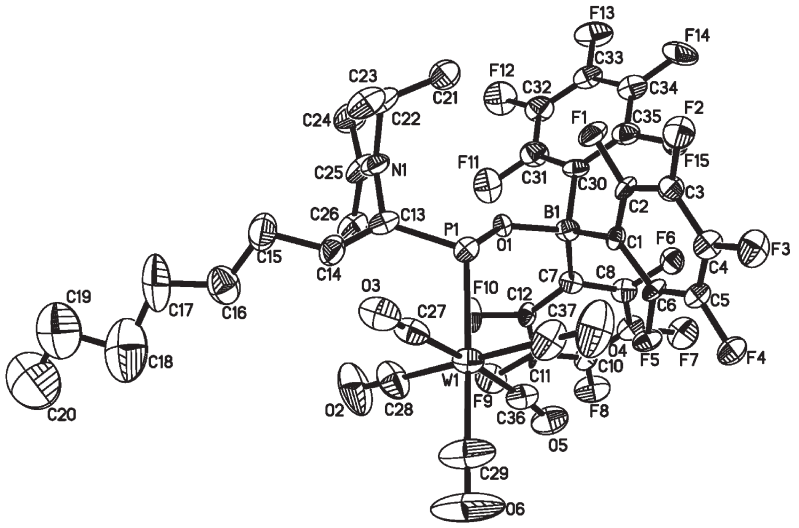


Figure 4. X-ray crystal structure analysis of secondary phosphine complex **14**a. Significant distances (Å) and angles (deg): P1−C13 1.867(10), P1−O1 1.63(2), O1−B1 1.520(14), P1−W1 2.484(12), C13−N1 1.471(13), N1−C25 1.327(11), N1−C221.520(12), C13−C14 1.322(14); O1−P1−C13 107.6(8), W1−P1−C13 109.1(4), W1−P1−O1 125.9(9), P1−C13−C14 127.5(9), P1−C13−N1 116.5(8), C14−C13−N1 116.0(9), C13−N1−C22 121.4(9), C13−N1−C25 118.4(10), C22−N1−C25 120.2(8).

J_{HP} = 346 Hz, J_{PW} = 298 Hz, major; δ^{31}P(**14**b) 59.9, J_{HP} = 337 Hz, J_{PW} = 302 Hz, minor) *syn*-crystallize, but it is possible to extract from the X-ray data the structural parameters of **14**a that are presented in Figure 4. The formation of **14** can be explained as follows: after complexation by the Lewis acid and cleavage of the P−C(Hex) ring bond, the strongly positive phosphorus abstracts a hydride from the amino group. This observation confirms the results of the computation and establishes that the first step of the mechanism of the ring expansion of phosphirenes to phosphindoles is the cleavage of the P−C(Ph) ring bond. Besides, it cast a serious doubt on the possibility to use such a route to prepare amino-stabilized phosphirenylium ions.

Experimental Section

General Procedure. NMR spectra were obtained on a JEOL ECA400 or JEOL ECA400SL spectrometer. All spectra were recorded at 298 K unless otherwise specified. Elemental analyses were performed in the Division of Chemistry and Biological Chemistry, Nanyang Technological University. HRMS spectra were obtained in ESI mode on a Finnigan MAT95XP HRMS system (Thermo Electron Corp.). X-ray crystallographic analyses were performed on a Bruker X8 APEX diffractometer. All reactions were performed under argon. Silica gel (230−400 mesh) was used for the chromatographic separations. All commercially available reagents were used as received from the suppliers.

Phosphirene Complex 2. The 1-aminophosphirane complex **1** (0.286 g, 0.6 mmol) and (phenylethynyl)(diisopropyl)amine (0.242 g, 1.2 mmol) were heated in 5 mL of toluene at 100 °C for 2 h. After evaporation of the solvent, the residue was chromatographed with hexane to give phosphirene as a colorless oil, **2** (0.238 g, 61%).

^{31}P NMR (162 MHz, $CDCl_3$): δ −97.8 (s, $^1J_{pw}$ = 306.8 Hz, $^2J_{PNH}$ = 26.3 Hz). ^{1}H NMR (400 MHz, $CDCl_3$, −50 °C): δ 7.54−7.38 (m, 4H, Ar*H*), 7.34−7.26 (m, 1H, Ar*H*), 7.11 (d, J = 7.4 Hz, 2H, Ar*H*), 6.90 (t, J = 7.4 Hz, 1H, Ar*H*), 6.75 (d, J = 7.8 Hz, 2H, Ar*H*), 4.23 (d, J = 22.9 Hz, 1H, N*H*), 4.04 (br sep, 1H, C*H*), 3.60 (br sep, 1H, C*H*), 1.35 (d, J = 6.4 Hz, 3H, CH_3), 1.32 (d, J = 6.9 Hz, 3H, CH_3), 1.11 (d, J = 6.4 Hz, 3H, CH_3), 1.04 (d, J = 6.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, −50 °C): δ 199.0 (d, J = 33.5 Hz, *trans* CO), 196.3 (d, J = 8.6 Hz, *cis* CO), 141.9 (d, J = 11.5 Hz, =C(N)), 136.2 (d, J = 22.4 Hz, *ipso* PhN), 130.9 (s, *ipso* ArC), 130.0 (4 × ArCH), 127.9 (s, ArCH), 127.8 (s, ArCH), 126.4 (s, ArCH), 122.1 (s, ArCH), 120.0 (2× ArCH), 96.8 (d, J = 9.6 Hz, =C (ArC-P)), 54.3 (CH), 47.7 (CH), 25.5 (CH_3), 22.0 (CH_3), 21.5 (CH_3), 21.2 (CH_3). Exact mass: calcd for $C_{25}H_{25}N_2O_5PW$ 648.1010; found 648.1016.

Phosphirene Complex 12. The 1-aminophosphirane complex **1** (0.237 g, 0.5 mmol) and *N,N*-diisopropyloct-1-yn-1-amine (0.222 g, 1.0 mmol) were heated in 5 mL of toluene at 110 °C for 4 h. After evaporation of the solvent, the residue was chromatographed at −5 °C with hexane to give phosphirene as a colorless oil, **12** (0.204 g, 62%).

^{31}P NMR (162 MHz, $CDCl_3$): δ −101.0 (s, $^1J_{pw}$ = 308.3 Hz). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (t, J = 8.2 Hz, 2H, Ar*H*), 6.94 (t, J = 7.4 Hz, 1H, Ar*H*), 6.74 (d, J = 7.7 Hz, 2H, Ar*H*), 4.00 (d, $^2J_{PH}$ = 22.7 Hz, N*H*), 3.74 (br s, 2H, 2 × C*H*), 2.49−2.42 (m, 2H, CH_2), 1.67−1.59 (m, 2H, CH_2), 1.42−1.30 (m, 6H, 3 × CH_3), 1.29−1.19 (m, 12H, 4 × CH_3), 0.90 (t, J = 6.8 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.0 (d, J = 32.0 Hz, *trans* CO), 196.5 (d, J = 9.6 Hz, *cis* CO), 142.1 (d, J = 11.3 Hz, =C(N)), 137.7 (d, J = 12.1 Hz, *ipso* C(PhNH)), 128.7 (s, *meta* CH(Ph)), 121.9 (s, *ortho* CH(Ph), 120.5 (s, *para* CH(Ph)), 98.4 (d, J = 2.5 Hz, =C), 31.4 (CH_2), 29.2 (CH_2), 28.3 (d, J = 3.6 Hz, CH_2), 26.8 (d, J = 3.1 Hz, CH_2), 22.5 (CH_2), 21.8 (4 × CH_3), 14.0 (CH_3). Exact mass: calcd for $C_{25}H_{33}N_2O_5PW$ 656.1636; found 656.1658.

Complexes 4 and 5. The 7-β-chloroethyl-7-phosphanorbornadiene complex[9] (0.320 g, 0.50 mmol) and *N*-isopropyl-*N*-(phenylethynyl)propan-2-amine (0.201 g, 1.0 mmol) were heated in 5 mL of toluene with a small amount of CuCl at 60 °C for 1 h. After evaporation of the solvent, the residue was chromatographed with hexane−ethyl acetate (90:10) to give phosphirene **4** (0.064 g, 21%) and diphosphetene **5** (0.054 g, 21%) as colorless oils.

Phosphirene 4. ^{31}P NMR (122 MHz, CD_2Cl_2): δ −143.6 (s, $^1J_{pw}$ = 266.0 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.54 (d, J = 7.9 Hz, 2H, *ortho* Ar*H*), 7.43 (t, J = 7.5 Hz, 2H, *meta* Ar*H*), 7.28 (t, J = 6.7 Hz, 1H, *para* Ar*H*), 4.03 (sep, 2H, 2 × C*H*), 3.45−3.36 (m, 2H, CH_2Cl), 2.42−2.34 (m, 2H, CH_2), 1.44 (d, J = 6.8 Hz, 6H, 2 × CH_3), 1.39 (d, J = 7.1 Hz, 6H, 2 × CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.8 (d, J = 29.5 Hz, *trans* CO), 196.4 (d, J = 8.4 Hz, *cis* CO), 141.3 (d, J = 17.0 Hz, =C(N)), 130.6 (s, *ipso* ArC), 128.8 (s, *meta* ArCH), 127.9 (d, J = 6.4 Hz, *ortho* ArCH), 126.4 (s, *para* ArCH), 114.1 (s, =CP), 52.1 (CH), 52.0 (CH), 42.5 (d, J = 13.2 Hz, CH_2), 40.3 (CH_2), 22.5 (2 × CH_3), 22.0

(2 × CH_3). Exact mass: calcd for $C_{21}H_{23}ClNO_5PW$ 619.0512, found 619.0523.

Diphosphetene 6. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 39.1 (d, $^1J_{PW}$ = 229.4 Hz, $\sum J_{PP}$ = 24.3 Hz), 2.90 (d, $^1J_{PW}$ = 243.6 Hz, $\sum J_{PP}$ = 23.7 Hz). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.43 (t, J = 7.5 Hz, 2H, Ar*H*), 7.39−7.35 (m, 1H, Ar*H*), 7.23 (t, J = 8.2 Hz, 2H, Ar*H*), 3.91−3.87 (m, 4H, 2 × C*H*, CH_2Cl), 3.86−3.82 (m, 2H, CH_2Cl), 3.26−3.10 (m, 2H, CH_2), 3.09−2.98 (m, 2H, CH_2), 1.37 (d, J = 7.1 Hz, 6H, 2 × CH_3), 1.32 (d, J = 6.7 Hz, 6H, 2 × CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 196.9 (d, J = 26.1 Hz, *trans* CO), 196.3 (d, J = 26.8 Hz, *trans* CO), 195.7 (d, J = 5.8 Hz, *cis* CO), 195.5 (d, J = 6.7 Hz, *cis* CO), 150.6 (dd, J = 20.8 and 33.0 Hz, P-C-N), 137.2 (d, J = 9.5 Hz, *ipso* ArC), 137.0 (d, J = 10.2 Hz, *ipso* ArC), 129.0 (2 × ArCH), 128.5 (ArCH), 128.4 (ArCH), 128.3 (ArCH), 114.8 (dd, J = 20.0 and 39.0 Hz, =CP), 53.7 (CH), 53.6 (CH), 43.8 (2 × CH_2), 41.0 (2 × CH_2), 23.6 (2 × CH_3), 22.0 (2 × CH_3). Exact mass: calcd for $C_{28}H_{27}Cl_2NO_{10}P_2W_2$ 1036.9506, found 1036.9491.

Phosphindole Complex 3. Phosphirene **2** (9 mg, 0.014 mmol) was dissolved in 2 mL of CH_2Cl_2, $B(C_6F_5)_3$ (11 mg, 0.021 mmol) was added into the reaction flask at 0 °C, and the mixture was stirred for 30 min. After evaporation of the solvent, the residue was purified by flash column chromatography on silica gel with 80:20 hexane−ethyl acetate then CH_2Cl_2 to give **3** (0.007 g, 46%) as white crystals.

^{31}P NMR (162 MHz, $CDCl_3$): δ 98.9 (s, J_{pw} = 311.1 Hz). ^1H NMR (400 MHz, $CO(CD_3)_2$): δ 7.61−7.58 (t, J = 7.6 Hz, 1H, ArC*H*), 7.46−7.39 (m, 3H, ArC*H*), 5.46 (m, 1H, C*H*(CH_3)$_2$), 4.95 (m, 1H, C*H*(CH_3)$_2$), 4.90−4.73 (m, 2H, CH_2), 1.84 (m, 9H, 3 × CH_3), 1.14 (d, J = 6.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CO(CD_3)_2$): δ 198.6 (d, J = 26.8 Hz, *trans* CO), 198.0 (br, C=N+), 196.0 (d, J = 7.9 Hz, *cis* CO), 147.7 (br d, J_{CF} = 235.8 Hz, *ortho* ArCF), 139.1 (d, J_{CF} = 246.9 Hz, *para* ArCF), 139.3 (d, J = 45.9 Hz, benzo-CP), 136.6 (br d, J = 247.3 Hz, *meta* ArCF), 132.0 (br s, *ipso* CArB), 131.5 (s, ArCH), 128.0 (d, J = 10.0 Hz, ArCH), 127.8 (d, J = 17.6 Hz, ArCH), 125.6 (d, J = 4.0 Hz, ArCH), 64.6 (d, J = 6.9 Hz, NCH), 57.8 (s, NCH), 36.84 (d, J = 11.5 Hz, CH_2), 20.49, 18.84, 18.65, 18.25 (4s, 4×CH_3).

Model Procedure for the Preparation of Phosphindoles 6, 9, and 10. Phosphirene **7** (0.063 g, 0.10 mmol) was dissolved in 5 mL of CH_2Cl_2, and $AlCl_3$ (14.7 mg, 0.11 mmol) was then added and stirred at room temperature for 30 min. After evaporation of the solvent, CH_2Cl_2 was added and the solid was removed by filtration. The residue was chromatographed on silica gel with hexane−ethyl acetate (80:20) to give phosphindole **9** as white crystals.

Phosphindole 6. Yield: 25 mg (40%). ^{31}P NMR (162 MHz, $CDCl_3$): δ 5.2 (s, $^1J_{PW}$ = 228.2 Hz, $^2J_{PH}$ = 22.5 Hz). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.38 (t, J = 7.6 Hz, 1H, Ar*H*), 7.27 (tt, J = 7.6, 1.2 Hz, 1H, Ar*H*), 7.09 (d, J = 7.6 Hz, 1H, Ar*H*), 7.05 (m, J = 7.4, 3.5, 1.0 Hz, 1H, Ar*H*), 5.86 (d, J = 22.5 Hz, 1H, C*H*), 3.94 (sep, 2H, 2 × C*H*), 3.40−3.32 (m, 1H, C*H*HCl), 3.09−3.01 (m, 1H, C*H*H), 2.73−2.70 (m, 2H, CH_2), 1.40 (d, J = 6.7 Hz, 6H, 2 × CH_3), 1.38 (d, J = 6.8 Hz, 6H, 2 × CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2 (d, J = 20.8 Hz, *trans* CO), 196.1 (d, J = 6.8 Hz, *cis* CO), 153.7 (d, J = 49.7 Hz, P-*C*-N), 146.4 (d, J = 9.6 Hz, *C*-CP), 135.0 (d, J = 50.6 Hz, *C*-P), 131.0 (ArCH), 127.4 (d, J = 15.2 Hz, ArCH), 122.1 (d, J = 10.2 Hz, ArCH), 120.0 (d, J = 5.1 Hz, ArCH), 104.8 (d, J = 14.2 Hz, *C*H-CP), 52.6 (CH), 52.5 (CH), 39.0 (d, J = 6.6 Hz, CH_2), 35.6 (d, J = 14.7 Hz, CH_2), 20.6 (2 × CH_3), 20.0 (2 × CH_3). Exact mass: calcd for $C_{21}H_{23}ClNO_5PW$ 619.0512, found 619.0518.

Phosphindole 9. Yield: 0.039 g (62%). ^{31}P NMR (162 MHz, $CDCl_3$): δ 14.7 (s, $^1J_{PW}$ = 229.3 Hz). ^1H NMR (400 MHz, $CDCl_3$): δ 7.62−7.57 (m, 2H, Ar*H*), 7.45−7.37 (m, 3H, Ar*H*), 7.22 (t, J = 7.5 Hz, 1H, Ar*H*), 7.16−7.10 (m, 2H, Ar*H*), 6.90 (td, J = 8.0, 3.9 Hz, 1H, Ar*H*), 5.78 (d, J = 22.4 Hz, 1H, C*H*), 3.73 (sep, 2H, 2 × C*H*), 1.33 (d, J = 6.7 Hz, 12H, 4 × CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2 (d, J = 23.2 Hz, *trans* CO), 196.4 (d, J = 6.9 Hz, *cis* CO), 155.9 (d, J = 50.0 Hz, P-*C*-N), 146.2 (d, J = 13.6 Hz, *C*-CP), 136.8 (d, J = 52.3 Hz, *C*-P), 133.2 (ArCH), 133.0 (ArCH), 131.3 (d, J = 2.6 Hz, ArCH), 130.6 (ArCH), 130.5 (d, J = 36.4 Hz, *ipso* ArC), 129.1 (ArCH), 129.0 (ArCH), 127.9 (d, J = 14.5 Hz, ArCH), 122.1 (d, J = 10.9 Hz, ArCH), 119.8 (d, J = 3.8 Hz, ArCH), 102.3 (d, J = 11.1 Hz, *C*H-CP), 50.4 (CH), 46.4 (CH), 20.3 (2 × CH_3), 19.8 (2 × CH_3). Exact mass: calcd for $C_{25}H_{24}NO_5PW$ 633.0901, found 633.0904.

Phosphindole 11. Yield: 0.033 g (56%). ^{31}P NMR (162 MHz, $CDCl_3$): δ 118.9 (s, $^1J_{pw}$ = 280.3 Hz). ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (t, J = 7.5 Hz, 1H, Ar*H*), 7.22 (t, J = 7.6 Hz, 1H, Ar*H*), 6.99 (td, J = 7.4, 4.0 Hz, 1H, Ar*H*), 6.93 (dd, J = 7.6, 2.2 Hz, 1H, Ar*H*), 5.69 (d, J = 22.9 Hz, 1H, C*H*), 4.11 (br s, 2H, 2 × C*H*), 3.37 (d, J = 12.1 Hz, 3H, OCH_3), 1.39 (d, J = 6.8 Hz, 6H, 2 × CH_3), 1.35 (d, J = 6.8 Hz, 6H, 2 × CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.7 (d, J = 27.0 Hz, *trans* CO), 196.1 (d, J = 7.6 Hz, *cis* CO), 155.4 (d, J = 53.4 Hz, P-*C*-N), 144.8 (d, J = 14.3 Hz, *C*-CP), 137.5 (d, J = 48.7 Hz, *C*-P), 132.5 (ArCH), 128.4 (d, J = 17.6 Hz, ArCH), 122.7 (d, J = 7.6 Hz, ArCH), 119.8 (d, J = 2.9 Hz, ArCH), 103.3 (d, J = 18.1 Hz, *C*H-CP), 55.3 (d, J = 13.4 Hz, OCH_3), 21.2 (CH_3), 20.5 (CH_3). Exact mass: calcd for $C_{20}H_{22}NO_6PW$ 587.0694, found C, 587.0696.

Aniline−Borane Adduct 13 and Secondary Phosphine Complexes 14a,b. Phosphirene **12** (0.145 g, 0.22 mmol) was dissolved in 8 mL of CH_2Cl_2, $B(C_6F_5)_3$ (0.169 g, 0.33 mmol) was added into the reaction flask at 0 °C, and the mixture was stirred for 30 min. After evaporation of the solvent, the residue was chromatographed on silica gel with 80:20 hexane−ethyl acetate to give the B−N adduct **13** then with CH_2Cl_2 to give **14**, both as white crystals.

Adduct yield: 0.081 g (61%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.30−7.22 (m, 3H, overlapping *meta* and *para* ArC*H*), 7.20 (br s, 2H, NH_2), 7.08−7.02 (m, 2H, *ortho* ArC*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.7 (d, J = 238.0 Hz, *ortho* ArCF), 140.3 (d, J = 250.0 Hz, *para* ArCF), 137.23 (d, J = 247.0 Hz, *meta* ArCF), 134.3 (s, *ipso* ArC), 129.8 (s, 2×ArCH), 129.0 (s, ArCH), 122.4 (s, 2 × ArCH), 116.1 (br s, BArC). ^{19}F NMR (376 MHz, $CDCl_3$): δ −133.04 (d, $^3J_{FF}$ = 20.0 Hz, 6F, *ortho* ArCF), −155.6 (t, $^3J_{FF}$ = 21.4 Hz, 3F, *para* ArCF), −162.4 (td, $^3J_{FF}$ = 24.4, 7.6 Hz, 6F, *meta* ArCF). Anal. Calcd for $C_{24}H_7BF_{15}N$: C, 47.64; H, 1.17; N, 2.31. Found: C, 47.65; H, 1.06 ; N, 2.31.

Yield of 14: 0.06 g (25%). ^{31}P NMR (162 MHz, $CDCl_3$): δ 68.8 (s, J_{PW} = 298.0 Hz, J_{PH} = 346.2 Hz, major isomer), 59.9 (s, J_{PW} = 302.4 Hz, J_{PH} = 337.4 Hz, minor isomer). Selected ^{13}C NMR data (400 MHz, $CDCl_3$, major isomer): δ 195.84 (d, J = 8 Hz, *cis* CO), 192.0 (s, C=N+), 147.8 (d, J = 28 Hz, =CH). ^{19}F NMR (376 MHz, $CDCl_3$): δ −132.33 (d, $^3J_{FF}$ = 23.1 Hz, 6F, minor isomer of *ortho* ArCF), −132.6 (d, $^3J_{FF}$ = 24.7 Hz, 6F, major isomer of *ortho* ArCF), −158.6 (t, $^3J_{FF}$ = 22.3 Hz, 3F, minor isomer of *para* ArCF), −158.9 (t, $^3J_{FF}$ = 21.6 Hz, 3F, major isomer of *para* ArCF), −164.4 (m, 6F, *meta* ArCF).

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Supporting Information Available: X-ray crystal structure analysis of compounds **3**, **9**, and **14**a. This material is available free of charge via the Internet at http://pubs.acs.org.