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Synthesis of Phosphaformamidines and Phosphaformamidinates

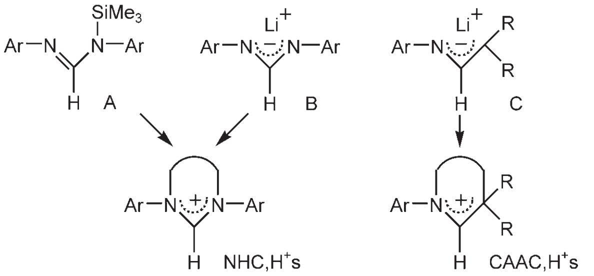
Maoying Song, Bruno Donnadieu, Michele Soleilhavoup, and Guy Bertrand*[a]

Abstract: A large-scale synthetic route to a variety of phosphaformamidines and phosphaformamidinates, a type of derivative that was not accessible by the methods previously known for preparing phosphaamidines and phosphaamidinates, is reported. Thermally stable ethyl *N*-arylformimidates **1** (ArN=CH(OEt), Ar = 2,4,6-$(Me)_3Ph$ or 2,6-$(iPr)_2Ph$) readily reacted with lithium dialkyl- and diarylphosphanides to afford the corresponding *N*-aryl phosphaformamidines in 80 and 60 % yield, respectively, whereas with lithium (aryl)(silyl)phosphanide, the *N*-aryl-*N*-silylphosphaformamidine (60 % yield) was obtained. Addition of primary lithium arylphosphanides to **1** followed by addition of a stoichiometric amount of *n*BuLi gave rise to the respective phosphaformamidinates (70–88 % yield). Methanolysis of the products afforded the *N*-aryl-*N*-hydrogenophosphaformamidines (90–95 % yield). The solid-state structure of one of the phosphaformamidinates is also presented.

Keywords: carbene precursors · formamidines · lithium · phosphaalkenes · phosphorus

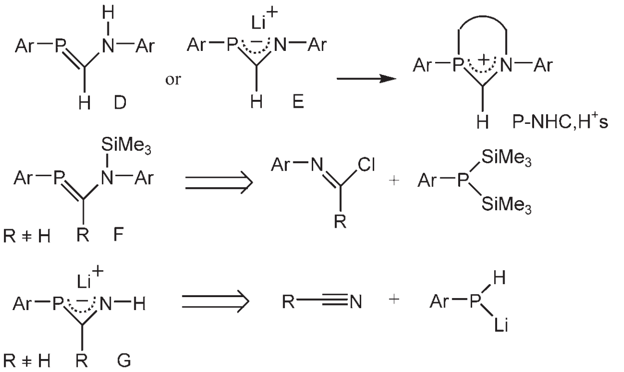
Introduction

Amidines and the corresponding amidinates have attracted considerable attention as ancillary ligands for main-group elements, transition metals, and lanthanides.[1] They have been used as substitutes for cyclopentadienyl ligands and have led to active catalysts for ring-opening polymerization[2] as well as olefin polymerization.[3] Recently, it was shown that *N*-silyl formamidines A[4a] and formamidinates B[4b] can also be used for the highly efficient synthesis of protonated N-heterocyclic carbenes (NHC,H$^+$s), the classical precursors for the widely used NHCs[5] (Scheme 1). Similarly, we showed that azaallyl anions C can be used for the preparation of aldiminium salts,[4,6] the immediate precursors of cyclic (alkyl)(amino)carbenes (CAACs)[7] (Scheme 1).



Scheme 1. *N*-Silylformamidines A, formamidinates B, and azaallyl anions C are direct precursors of protonated NHCs and CAACs.

With this in mind, we became interested in monophosphorus analogues D and E of formamidines and formamidinates, respectively, as potential starting materials for yet unknown P,N-heterocyclic carbenes (P-NHCs) (Scheme 2). Few examples of phosphaamidines F[8] and phosphaamidinates G[9] (R ≠ H) have been reported, beginning with the seminal work by Issleib et al.,[8a] who treated bis-silylated



Scheme 2. Phosphaformamidines and -formamidinates as potential precursors for protonated P-NHCs: known retrosynthetic approaches to phosphaamidines and -amidinates (R ≠ H).

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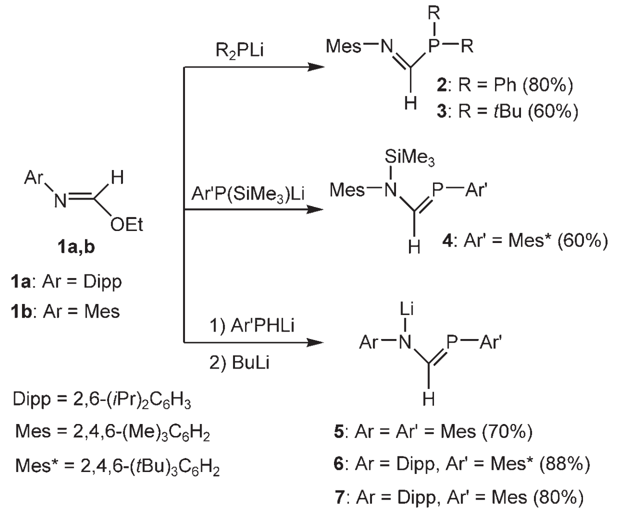
phosphines with imide chlorides. Niecke and co-workers[9a] synthesized a lithium phosphaamidinate by addition of lithium phenylphosphanide[10] to acetonitrile. More recently, several variants of these two synthetic routes have been published, but all of them involve either a nitrile and a phosphide or an imide chloride as starting materials.[8,9,11] Clearly, none of these synthetic approaches can be used for the preparation of phosphaformamidines D and -formamidinates E, as on the one hand formimide chlorides [H(Cl)N=CR] are unstable, and on the other hand phosphide would deprotonate hydrogen cyanide.

Herein we report the synthesis of the first phosphaformamidines D and phosphaformamidinates E as well as the solid-state structure of a lithium phosphaformamidinate.

Results and Discussion

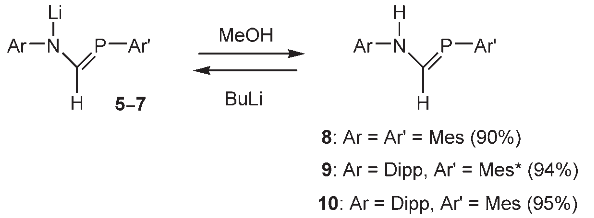
Among the possible precursors, we chose *N*-aryl formimidates **1** (Scheme 3), which, in marked contrast with formimide chlorides, are thermally very stable.[12] Derivatives **1a** and **1b**, which feature a bulky aryl substituent at nitrogen, were readily prepared in large quantities by addition of the desired primary aryl amine to ethyl orthoformate, with the procedure described by DeWolfe.[12a] To test the possibility of a substitution reaction with a phosphorus nucleophile, formimidate **1b** was treated with a stoichiometric amount of lithium diphenylphosphide in Et_2O. The reaction was complete in one hour at ambient temperature, and phosphaformamidine **2** was isolated in 80 % yield (Scheme 3). This reaction can also be performed with a bulky secondary phosphide, as **1b** also reacted at room temperature with lithium di-*tert*-butylphosphide to afford **3** in 60 % yield.



Scheme 3. Synthesis of phosphaformamidines **2**–**4** and phosphaformamidinates **5**–**7**.

As N-silylated 1,3-diazaallyl anions are of special importance as chelating ligands and as building units for constructing new NHCs, we investigated the reaction of a formimidate with a sterically crowded silyl phosphide. Indeed, lithium [2,4,6-tris(*tert*-butyl)phenyl](trimethylsilyl)phosphide reacted at room temperature with **1b**, and after workup *N*-silylphosphaformamidine **4** was isolated in 60 % yield (Scheme 3).[13] Not surprisingly, when the reaction was monitored by ^{31}P NMR spectroscopy at −50 °C, no evidence for the *P*-silyl phosphaformamidine isomer was found.

When one equivalent of primary lithium arylphosphide was added to **1a** or **1b**, the expected phosphaformamidines **8**–**10** (Scheme 4) were not formed; instead, 1:1 mixtures of lithium phosphaformamidinates **5**–**7** and arylphosphines ($ArPH_2$) were observed by ^{31}P NMR spectroscopy (Scheme 3). Clearly, primary phosphides are basic enough to deprotonate phosphaformamidines **8**–**10**. However, we discovered that the addition of another equivalent of butyl lithium to the reaction mixture consumed completely the primary arylphosphines and the unreacted *N*-aryl formimidates **1** to afford phosphaformamidinates **5**–**7** as the *E-syn*-(P=C) isomers, which were isolated in good yields as yellow powders (Scheme 3).



Scheme 4. Synthesis of phosphaformamidines **8**–**10** by protonation of phosphaformamidinates **5**–**7**, and deprotonation of the latter to afford the former.

Light-yellow crystals of **6** were obtained after recrystallization from THF at −30 °C and were subjected to single-crystal X-ray diffraction (Figure 1). The lithium ion is coordinated to the nitrogen atom, and the highly delocalized structure is confirmed by the co-planarity of C2, N, C1, P, and C14, as well as the relatively long P−C1 bond (1.735 Å).

Phosphaformamidines **8**–**10** can be readily prepared in high yields by addition of an excess of methanol to phosphaformamidinates **5**–**7** (Scheme 4). Clearly, derivatives **8**–**10** can be cleanly deprotonated with BuLi to reproduce the salts **5**–**7**.

Conclusions

In summary, we have developed a large-scale synthetic route to a variety of phosphaformamidines D and phosphaformamidinates E, a type of derivative that was not accessible by the methods previously known for preparing phosphaamidines F and phosphaamidinates G. The use of derivatives of types D and E for the preparation of the protonated form of P-NHCs is under active investigation.

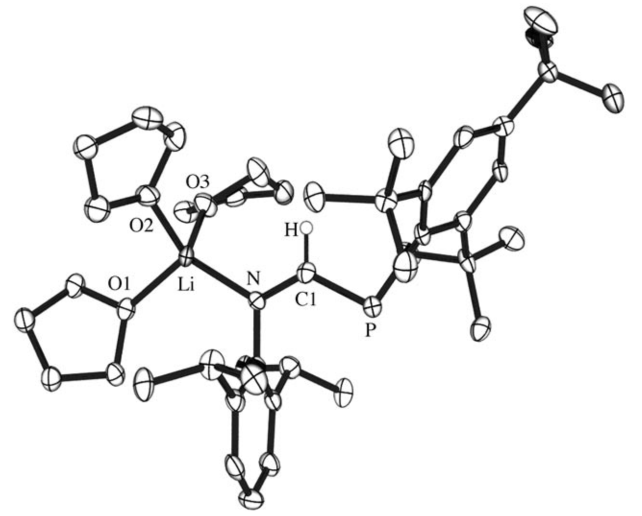


Figure 1. X-ray crystal structure of **6** (H atoms, except those on the allyl carbon atom, are omitted for clarity). Selected bond lengths (Å) and angles (°): P–C1 1.735(7), N–C1 1.318(9), N–Li 2.018(14), Li–O1 1.957(16), Li–O2 1.935(14), Li–O3 1.954(15), N–C2 1.416(9), P–C14 1.874; C1-P-C14 101.1(3), P-C1-N 128.9(6), C1-N-C2 115.7(6), C1-N-Li 124.8(6), C2-N-Li 119.5(6), N-Li-O1 115.6(7), N-Li-O3 113.4(6), N-Li-O2 115.0(7), O1-Li-O2 107.5(7), O2-Li-O3 101.3(6), O1-Li-O3 102.4(8).

Experimental Section

General

All manipulations were performed under an inert atmosphere of argon with standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Varian Inova 300, 500 and Bruker Avance 300 spectrometers. The high purity of all isolated products was confirmed by multinuclear NMR spectroscopy. Mass spectroscopic analysis was performed in multimode and recorded on an Agilent LC TOF spectrometer.

Syntheses

1a: A mixture of 2,6-diisopropylaniline (47 g, 0.265 mol) and triethyl orthoformate (71 g, 0.479 mol) was heated at 140 °C for 3 h, and then at 170 °C, until the theoretical quantity of ethanol was collected. The crude product was distilled under vacuum to afford ethyl *N*-2,6-di-*iso*-propylphenylformimidate (**1a**) as a light yellow oil (50.7 g, 82 %). B.p.: 95–98 °C (0.1 mbar); ^{1}H NMR (CDCl$_3$, 25 °C): $\delta = 1.35$ (d, $^3J_{\mathrm{H,H}} = 7.2$ Hz, 12 H, CHC*H*$_3$), 1.59 (t, $^3J_{\mathrm{H,H}} = 7.2$ Hz, 3 H, CH$_2$C*H*$_3$), 3.20 (sept, $^3J_{\mathrm{H,H}} = 7.2$ Hz, 2 H, C*H*CH$_3$), 4.57 (q, $^3J_{\mathrm{H,H}} = 7.2$ Hz, 2 H, C*H*$_2$CH$_3$), 7.20–7.30 (m, 3 H, H$_{\mathrm{arom}}$), 7.62 ppm (s, 1 H, C*H*OEt); ^{13}C NMR (CDCl$_3$, 25 °C): $\delta = 14.2$ (s, CH$_2$*C*H$_3$), 23.4 (s, CH*C*H$_3$), 27.9 (s, *C*HCH$_3$), 61.6 (s, *C*H$_2$CH$_3$), 122.8 (s, CH$_{\mathrm{arom}}$), 123.7 (s, CH$_{\mathrm{arom}}$), 139.1 (s, C$_{\mathrm{arom}}$), 143.5 (s, *ipso*-C), 153.7 ppm (s, *C*HOEt).

1b: By using the same procedure as above, but with 2,4,6-trimethylaniline (9.63 g, 0.071 mol) and triethyl orthoformate (16.0 g, 0.108 mol), ethyl *N*-mesityl-formimidate (**1b**) was obtained as a light-yellow oil (8.96 g, 66 %). B.p.: 85–88 °C (0.1 mbar); ^{1}H NMR (C$_6$D$_6$, 25 °C): $\delta = 1.12$ (t, $^3J_{\mathrm{H,H}} = 6.9$ Hz, 3 H, CH$_2$C*H*$_3$), 2.02 (s, 6 H, CCH$_3$), 2.13 (s, 3 H, CCH$_3$), 4.18 (q, $^3J_{\mathrm{H,H}} = 6.9$ Hz, 2 H, C*H*$_2$CH$_3$), 6.71 (s, 2 H, H$_{\mathrm{arom}}$), 7.10 ppm (s, 1 H, C*H*OEt); ^{13}C NMR (C$_6$D$_6$, 25 °C): $\delta = 14.7$ (s, *C*H$_3$CH$_2$), 18.9 (s, C*C*H$_3$), 21.2 (s, C*C*H$_3$), 62.0 (s, CH$_3$*C*H$_2$), 128.9 (s, C$_{\mathrm{arom}}$) 129.4 (s, CH$_{\mathrm{arom}}$), 132.4 (s, C$_{\mathrm{arom}}$), 144.4 (s, C$_{\mathrm{arom}}$), 155.2 ppm (s, *C*HOEt).

2: Lithium diphenylphosphide (0.514 g, 2.68 mmol) was dissolved in Et$_2$O (10 mL), and the mixture was added to a solution of **1b** (0.510 g, 2.67 mmol) in Et$_2$O (2 mL). The solution was stirred at room temperature for 1.5 h, the solvent was removed under vacuum, and the residue was extracted with hexane. Evaporation of hexane afforded *N*-2,4,6-trimethylphenyl-*P*-diphenylphosphaformamidine (**2**) as a 90:10 mixture of *E* and *Z* isomers in the form of a light-yellow oil (0.708 g, 80 %). ^{1}H NMR (C$_6$D$_6$, 25 °C): *E* isomer: $\delta = 2.19$ (s, 6 H, CCH$_3$), 2.30 (s, 3 H, CCH$_3$), 6.87 (s, 2 H, H$_{\mathrm{arom}}$), 7.24–7.29 (m, 8 H, H$_{\mathrm{arom}}$), 7.71–7.77 (m, 2 H, H$_{\mathrm{arom}}$), 8.60 ppm (d, $^2J_{\mathrm{P,H}} = 38.1$ Hz, 1 H, NCHP); *Z* isomer: 9.26 ppm (d, $^2J_{\mathrm{P,H}} = 18.0$ Hz, 1 H, NCHP); ^{13}C NMR (C$_6$D$_6$, 25 °C): *E* isomer: $\delta = 18.9$ (s, CH$_3$), 21.3 (s, CH$_3$), 126.8 (s, C$_{\mathrm{arom}}$), 129.3 (d, $^3J_{\mathrm{P,C}} = 7.1$ Hz, CH$_{\mathrm{arom}}$), 129.6 (s, CH$_{\mathrm{arom}}$), 129.8 (s, CH$_{\mathrm{arom}}$), 133.4 (s, C$_{\mathrm{arom}}$), 134.8 (d, $^2J_{\mathrm{P,C}} = 18.9$ Hz, CH$_{\mathrm{arom}}$), 135.5 (d, $^1J_{\mathrm{P,C}} = 9.1$ Hz, C$_{\mathrm{arom}}$), 151.4 (d, $^3J_{\mathrm{P,C}} = 9.8$ Hz, C$_{\mathrm{arom}}$), 174.7 ppm (d, $^1J_{\mathrm{P,C}} = 10.6$ Hz, NCHP); *Z* isomer: 172.9 ppm (d, $^1J_{\mathrm{P,C}} = 37.7$ Hz, NCHP); ^{31}P NMR (C$_6$D$_6$, 25 °C) $\delta = -5.9$ (*E*), -16.9 ppm (*Z*).

3: A solution of lithium di(*tert*-butyl)phosphide (0.510 g, 3.29 mmol) in THF (10 mL) was added to a solution of **1b** (0.630 g, 3.13 mmol) in THF (5 mL) at −75 °C. The light-orange solution was stirred at room temperature overnight, the solvent was removed under vacuum, and the resulting residue was extracted with hexane. Evaporation of hexane afforded *N*-2,4,6-trimethylphenyl-*P*-di-*tert*-butylphosphaformamidine (**3**; *E* isomer) as a yellow oil (0.547 g, 60 %). ^{1}H NMR (C$_6$D$_6$, 25 °C): $\delta = 1.27$ (d, $^3J_{\mathrm{P,H}} = 11.7$ Hz, 18 H, CCH$_3$), 2.11 (s, 6 H, CH$_3$), 2.18 (s, 3 H, CH$_3$), 6.76 (s, 2 H, H$_{\mathrm{arom}}$), 8.40 ppm (d, $^2J_{\mathrm{P,H}} = 32.7$ Hz, 1 H, NCHP); ^{13}C NMR (C$_6$D$_6$, 25 °C) $\delta = 18.8$ (s, Ar*C*H$_3$), 20.8 (s, Ar*C*H$_3$), 30.4 (d, $^2J_{\mathrm{P,C}} = 12.1$ Hz, PC*C*H$_3$), 32.9 (d, $^1J_{\mathrm{P,C}} = 20.8$ Hz, P*C*CH$_3$), 126.2 (s, C$_{\mathrm{arom}}$), 129.1 (s, CH$_{\mathrm{arom}}$), 132.4 (s, C$_{\mathrm{arom}}$), 152.1 (d, $^3J_{\mathrm{P,C}} = 6.3$ Hz, C$_{\mathrm{arom}}$), 174.3 ppm (d, $^1J_{\mathrm{P,C}} = 24.7$ Hz, NCHP); ^{31}P NMR (C$_6$D$_6$, 25 °C): $\delta = 34.8$ ppm.

4: A solution of lithium (2,4,6-tri-*tert*-butylphenyl)(trimethylsilyl)phosphide (0.642 g, 1.80 mmol) in Et$_2$O (10 mL) was added at room temperature to a solution of **1b** (0.380 g, 1.99 mmol) in Et$_2$O (5 mL). The solution was stirred at room temperature overnight, the solvent was removed under vacuum, and the resulting residue was extracted with hexane. Crystallization from hexane at −30 °C afforded *N*-(2,4,6-trimethylphenyl)-*N*-trimethylsilyl-*P*-(2,4,6-tri-*tert*-butylphenyl)methylidene phosphane (**4**) as colorless crystals (0.535 g, 60 %). ^{1}H NMR (C$_6$D$_6$, 25 °C): $\delta = -0.11$ (s, 9 H, SiCH$_3$), 1.33 (s, 9 H, CCH$_3$), 1.77 (s, 18 H, CCH$_3$), 2.13 (s, 3 H, CH$_3$), 2.38 (s, 6 H, CH$_3$), 6.87 (s, 2 H, H$_{\mathrm{arom}}$), 7.69 (d, $^4J_{\mathrm{P,H}} = 1.2$ Hz, 2 H, H$_{\mathrm{arom}}$), 8.24 ppm (d, $^2J_{\mathrm{P,H}} = 16.8$ Hz, 1 H, NCHP); ^{13}C NMR (C$_6$D$_6$, 25 °C): $\delta = 0.0$ (s, SiCH$_3$), 19.1 (s, Ar*C*H$_3$), 21.2 (s, Ar*C*H$_3$), 31.8 (s, ArC*C*H$_3$), 34.2 (d, $^4J_{\mathrm{P,C}} = 8.3$ Hz, ArC*C*H$_3$), 35.3 (s, Ar*C*CH$_3$), 39.2 (s, Ar*C*CH$_3$), 122.0 (s, CH$_{\mathrm{arom}}$), 130.4 (s, CH$_{\mathrm{arom}}$), 135.4 (s, C$_{\mathrm{arom}}$), 135.9 (d, $^1J_{\mathrm{P,C}} = 70.2$ Hz, C$_{\mathrm{arom}}$), 149.2 (s, C$_{\mathrm{arom}}$), 156.4 (d, $^2J_{\mathrm{P,C}} = 2.6$ Hz, C$_{\mathrm{arom}}$), 183.3 ppm (d, $^1J_{\mathrm{P,C}} = 45.6$ Hz, NCHP); ^{31}P NMR (C$_6$D$_6$, 25 °C) $\delta = 121.9$ ppm (d, $^2J_{\mathrm{P,H}} = 17.7$ Hz); signals corresponding to two aromatic quaternary carbon atoms were not observed.

5: BuLi (2.5 M solution in hexane, 10.1 mL, 0.025 mol) was added at −78 °C to a solution of MesPH$_2$ (3.23 g, 0.021 mol) in Et$_2$O (40 mL). After 30 min at low temperature, the orange solution was warmed to room temperature and then stirred for an additional 30 min. The resulting solution of MesPHLi was then added at −60 °C with a dropping funnel over 30 min to a solution of **1b** (4.46 g, 0.023 mol) in Et$_2$O (10 mL). After 45 min at low temperature, the red solution was warmed to room temperature and stirred overnight. The resulting dark-red solution was cooled to −78 °C, and BuLi (2.5 M solution in hexane, 10.1 mL, 0.025 mol) was added slowly with a syringe. The reaction mixture was stirred at low temperature for 45 min and then at room temperature overnight. The solvent was removed under vacuum, the residue washed three times with hexane (20 mL), and lithium *N*-(2,4,6-trimethylphenyl)-*P*-(2,4,6-trimethylphenyl)phosphaformamidinate (**5**) was obtained as a yellow powder (4.46 g, 70 %). ^{13}C NMR (THF, 25 °C): $\delta = 18.1$ (s, CH$_3$), 18.8 (s, CH$_3$), 20.3 (s, CH$_3$), 20.6 (d, $^3J_{\mathrm{P,C}} = 6.4$ Hz, CH$_3$), 127.1 (s, CH$_{\mathrm{arom}}$), 127.6 (d, $^1J_{\mathrm{P,C}} = 68.4$ Hz, C$_{\mathrm{arom}}$), 128.4 (s, CH$_{\mathrm{arom}}$), 129.2 (s, C$_{\mathrm{arom}}$), 129.9 (s, C$_{\mathrm{arom}}$), 130.0 (s, C$_{\mathrm{arom}}$), 131.9 (s, C$_{\mathrm{arom}}$), 142.4 (d, $^2J_{\mathrm{P,C}} = 8.7$ Hz, C$_{\mathrm{arom}}$), 191.9 ppm (d, $^1J_{\mathrm{P,C}} = 67.0$ Hz, NCHP); ^{31}P NMR (THF, 25 °C): $\delta = 23.8$ ppm.

6: By using the same procedure as for **5**, lithium *N*-(2,6-di-*iso*-propylphenyl)-*P*-(2,4,6-tri-*tert*-butylphenyl)phosphaformamidinate (**6**) was obtained as a yellow powder (8.72 g, 88 %); ^{13}C NMR (C$_6$D$_6$, 25 °C): $\delta = 25.4$ (s, CH*C*H$_3$), 26.8 (s, CH*C*H$_3$), 27.5 (s, *C*HCH$_3$), 32.3 (s, C*C*H$_3$), 34.4 (d, $^4J_{\mathrm{P,C}} = 9.2$ Hz, C*C*H$_3$), 39.6 (s, *C*CH$_3$), 39.8 (s, *C*CH$_3$), 120.8 (s, CH$_{\mathrm{arom}}$), 122.9 (s, CH$_{arom}$), 123.7 (s, CH$_{arom}$), 142.1 (s, C$_{arom}$), 142.6 (s, C$_{arom}$), 146.2 (s, C$_{arom}$), 148.3 (d, $^1J_{P,C}=65.0$ Hz, C$_{arom}$), 157.4 (s, C$_{arom}$), 193.0 ppm (d, $^1J_{P,C}=71.4$ Hz, NCHP); ^{31}P NMR (benzene, 25 °C): $\delta=46.8$ ppm.

7: By using the same procedure as for **5**, lithium *N*-(2,6-di-*iso*-propylphenyl)-*P*-(2,4,6-trimethylphenyl)phosphaformamidinate (**7**) was obtained as a yellow powder (5.80 g, 80 %). ^{13}C NMR (THF, 25 °C): $\delta=21.4$ (s, CH$_3$), 25.1 (s, CH$_3$), 25.7 (s, CH*C*H$_3$), 25.8 (s, CH*C*H$_3$), 28.3 (s, *C*HCH$_3$), 122.6 (s, CH$_{arom}$), 123.5 (s, CH$_{arom}$), 127.8 (s, CH$_{arom}$), 133.0 (s, C$_{arom}$), 141.9 (s, C$_{arom}$), 143.2 (d, $^2J_{P,C}=6.7$ Hz, C$_{arom}$), 147.2 (d, $^1J_{P,C}=48.8$ Hz, C$_{arom}$), 152.5 (d, $^4J_{P,C}=9.2$ Hz, C$_{arom}$), 194.9 ppm (d, $^1J_{P,C}=67.6$ Hz, NCHP); ^{31}P NMR (THF, 25 °C): $\delta=30.4$ ppm.

8: Anhydrous methanol (4.75 g, 0.148 mol) was added to a clear-orange solution of **5** (5.50 g, 0.018 mol) in THF (50 mL) at 0 °C, and the reaction mixture was stirred at room temperature overnight. The volatiles were removed under vacuum, and the residue was extracted with hexane (40 mL). After evaporation of hexane, *N*-(2,4,6-trimethylphenyl)-*P*-(2,4,6-trimethylphenyl)phosphaformamidine (**8**) was obtained as a light-yellow powder (4.82 g, 90 %). M.p.: 102–103 °C; ^{1}H NMR (C$_6$D$_6$, 25 °C): $\delta=1.89$ (s, 6 H, CH$_3$), 2.05 (s, 3 H, CH$_3$), 2.16 (s, 3 H, CH$_3$), 2.60 (s, 6 H, CH$_3$), 5.78 (d, $^3J_{H,H}=13.7$ Hz, 1 H, NH), 6.53 (s, 2 H, H$_{arom}$), 6.87 (s, 2 H, H$_{arom}$), 7.60 ppm (dd, $^3J_{H,H}=13.7$ Hz, $^2J_{P,H}=44.2$ Hz, 1 H, NCHP); ^{13}C NMR (C$_6$D$_6$, 25 °C): $\delta=18.5$ (s, CH$_3$), 21.2 (s, CH$_3$), 21.5 (s, CH$_3$), 23.0 (d, $^3J_{P,C}=7.5$ Hz, CH$_3$), 119.0 (s, C$_{arom}$), 124.6 (d, $^1J_{P,C}=39.1$ Hz, C$_{arom}$), 129.5 (s, CH$_{arom}$), 129.9 (s, CH$_{arom}$), 132.6 (s, C$_{arom}$), 135.1 (s, C$_{arom}$), 138.4 (s, C$_{arom}$), 143.1 (s, C$_{arom}$), 171.7 ppm (d, $^1J_{P,C}=66.3$ Hz, NCHP); ^{31}P NMR (C$_6$D$_6$, 25 °C): $\delta=55.6$ ppm (d, $^2J_{P,H}=44.2$ Hz); MS (ESI-APCI (atmospheric pressure chemical ionization)): *m*/*z* calcd for C$_{19}$H$_{25}$NP: 298.1725 [*M*+H]$^+$; found: 298.1722.

9: By using the same procedure as for **8**, *N*-(2,6-di-*iso*-propylphenyl)-*P*-(2,4,6-tri-*tert*-butylphenyl)phosphaformamidine (**9**) was obtained as a white powder (8.38 g, 94 %). M.p.: 105–106 °C; ^{1}H NMR (C$_6$D$_6$, 25 °C) $\delta=1.13$ (d, $^3J_{H,H}=6.9$ Hz, 12 H, CHC*H*$_3$), 1.41 (s, 9 H, CC*H*$_3$), 1.74 (s, 18 H, CCH$_3$), 3.05 (sept, $^3J_{H,H}=6.9$ Hz, 2 H, C*H*CH$_3$), 5.17 (d, $^3J_{H,H}=13.5$ Hz, 1 H, NH), 7.11 (s, 3 H, H$_{arom}$), 7.32 (dd, $^3J_{H,H}=13.5$ Hz, $^2J_{P,H}=45.0$ Hz, 1 H, NCHP), 7.57 ppm (s, 2 H, H$_{arom}$); ^{13}C NMR (C$_6$D$_6$, 25 °C): $\delta=24.3$ (s, CH*C*H$_3$), 27.6 (s, *C*HCH$_3$), 31.7 (s, C*C*H$_3$), 32.0 (d, $^4J_{P,C}=7.4$ Hz, C*C*H$_3$), 35.2 (s, *C*CH$_3$), 38.6 (s, *C*CH$_3$), 122.0 (s, CH$_{arom}$), 124.1 (s, CH$_{arom}$), 125.4 (s, CH$_{arom}$), 133.2 (d, $^1J_{P,C}=56.7$ Hz, C$_{arom}$), 137.5 (s, C$_{arom}$), 142.0 (s, C$_{arom}$), 149.5 (s, C$_{arom}$), 156.1 (s, C$_{arom}$), 166.9 ppm (d, $^1J_{P,C}=64.6$ Hz, NCHP); ^{31}P NMR (C$_6$D$_6$, 25 °C): $\delta=75.6$ (d, $^2J_{P,H}=45.6$ Hz); MS (ESI-APCI): *m*/*z* calcd for C$_{31}$H$_{49}$NP: 466.3603 [*M*+H]$^+$; found: 466.3616.

10: By using the same procedure as for **8**, *N*-(2,6-di-*iso*-propylphenyl)-*P*-(2,4,6-trimethylphenyl)phosphaformamidine (**10**) was obtained as a light-yellow powder (5.80 g, 95 %). M.p.: 104–105 °C; ^{1}H NMR (C$_6$D$_6$, 25 °C) $\delta=1.19$ (d, $^3J_{H,H}=6.8$ Hz, 12 H, CHC*H*$_3$), 2.28 (s, 3 H, CH$_3$), 2.80 (s, 6 H, CH$_3$), 3.27 (sept, $^3J_{H,H}=6.8$ Hz, 2 H, C*H*CH$_3$), 6.20 (d, $^3J_{H,H}=13.8$ Hz, 1 H, NH), 7.03–7.32 (m, 5 H, H$_{arom}$), 7.89 ppm (dd, $^3J_{H,H}=13.8$ Hz, $^2J_{P,H}=44.1$ Hz, 1 H, NCHP); ^{13}C NMR (C$_6$D$_6$, 25 °C): $\delta=21.5$ (s, CH$_3$), 22.9 (d, $^3J_{P,C}=8.4$ Hz, CH$_3$), 23.9 (s, CH*C*H$_3$), 28.9 (s, *C*HCH$_3$), 124.3 (s, CH$_{arom}$), 127.6 (s, CH$_{arom}$), 129.6 (s, CH$_{arom}$), 133.0 (d, $^1J_{P,C}=43.0$ Hz, C$_{arom}$), 138.6 (s, C$_{arom}$), 138.8 (s, C$_{arom}$), 143.1 (d, $^2J_{P,C}=5.0$ Hz, C$_{arom}$), 144.8 (s, C$_{arom}$), 173.1 ppm (d, $^1J_{P,C}=66.5$ Hz, NCHP); ^{31}P NMR (C$_6$D$_6$, 25 °C): $\delta=57.2$ ppm (d, $^2J_{P,H}=44.1$ Hz); MS (ESI-APCI): *m*/*z* calcd for C$_{22}$H$_{31}$NP: 340.2194 [*M*+H]$^+$; found: 340.2207.

Crystal-Structure Determination of 6

A Bruker X8-APEX X-ray diffraction instrument with Mo radiation was used for data collection of compound **6.** All data frames were collected at low temperature ($T=100$ K) with the ω,ϕ scan mode (0.3° ω-scan width, hemisphere of reflections) and integrated by using the Bruker SAINTPLUS software package. Intensity data were corrected for Lorentzian polarization. Absorption corrections were performed with the SADABS program. SIR97 was used for direct methods of phase determination, and the Bruker SHELXTL software package was used for structure refinement and difference Fourier maps. The atomic coordinates and the isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by full-matrix least-squares on F^2. All H atoms were included in the refinement in calculated positions riding on the C atoms, with U_{iso} fixed at 20 % higher than the isotropic parameters of the carbon atoms to which they were attached. Drawings of molecules were performed with Ortep 3. The crystal shows a racemic twin that could only be refined in the noncentrosymmetric space group *Cc* by using the following twin law: −1 0 0, 0 −1 0, 0 0 −1. A BASF parameter was also included in the refinement process. Crystal and structure parameters of **6**: size $=0.46\times0.14\times0.08$ mm^3, monoclinic, space group *Cc*, $a=10.434(4)$, $b=27.302(12)$, $c=16.421(6)$ Å, $\alpha=90.0$, $\beta=106.054(5)$, $\gamma=90.0°$, $V=4495(3)$ Å^3, $\rho_{calcd}=1.126$ g cm^{-3}, $2\theta_{max}=41.62°$, Mo radiation ($\lambda=0.71073$ Å), $T=100(2)$ K, reflections collected = 11 964, independent reflections = 6289 ($R_{int}=0.1077$, $R_{sig}=0.1875$), 3366 (53.5 %) reflections were greater than $2\sigma(I)$, index ranges $-11\leq h\leq 11$, $-30\leq k\leq 24$, $-18\leq l<18$, $\mu=0.0103$ mm^{-1}, max and min transmission = 0.9918 and 0.9541, respectively, 582 parameters were refined and converged at $R1=0.0723$, $wR2=0.1734$ with intensity $I>2\sigma(I)$, final difference peak and hole = 0.487 and −0.327 e Å^{-3}, respectively. CCDC-648460 (**6**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request.cif.

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