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Half-sandwich rare-earth metal tris(alkyl) ate complexes catalyzed phosphaguanylation reaction of phosphines with carbodiimides: an efficient synthesis of phosphaguanidines†

Wangyang Ma,[a] Ling Xu,[a] Wen-Xiong Zhang*[ab] and Zhenfeng Xi[a]

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The phosphaguanylation reaction of phosphines with carbodiimides catalyzed by half-sandwich yttrium tris(trimethylsilylmethyl) ate complexes is achieved for the first time to efficiently prepare phosphaguanidines. The catalyst system of the yttrium ate complex displays better catalytic activity than those of neutral yttrium complexes.

Introduction

The catalytic guanylation reaction of amines with carbodiimides (CGAC reaction) has become a hot area of research, because it provides a straightforward and atom-economical route to prepare guanidines (RN═C(NR′R″)NHR).[1–3] In contrast, the catalytic phosphaguanylation reaction of phosphines with carbodiimides (hereafter as CPPC reaction), which is also known as catalytic addition of phosphines to carbodiimides or hydrophosphination of carbodiimides, has received considerably less attention, although this reaction provides an atom-economical synthesis of phosphaguanidines ($R'_2PC(=NR)NHR$). These phosphaguanidines, as analogues of guanidines, are widely used as building blocks of ancillary ligands for many transition metal species.[4,5] Initially, this catalyst-free direct phosphaguanylation reaction of diphenylphosphine with an *N*,*N*′-diaryl substituted carbodiimide was reported to afford the phosphaguanidine in a low yield under rather harsh conditions.[6] Recently, the direct phosphaguanylation reaction of the active hydrogen heptaphosphide dianion $[HP_7]^{2-}$ with RN═C═NR (R = 2,6-diisopropylphenyl (Dipp), iPr, and Cy) was reported to afford the functionalized cluster anions $[P_7C(=NR)NHR]^{2-}$.[7] Very recently, the stoichiometric NaH-mediated phosphaguanylation of phosphine boranes with carbodiimides provided an alternative synthesis of phosphaguanidines by the removal of the borane using 1,4-diazabicyclo[2.2.2]octane (DABCO).[8] The phosphaguanylation reaction of phosphines with the less electrophilic *N*,*N*′-dialkyl or *N*-alky-*N*′-aryl carbodiimides cannot be achieved without suitable catalysts; therefore, the search and design of suitable catalyst systems for the CPPC reaction are in high demand.

In 2006, Hou *et al.* reported the first CPPC reactions catalyzed *via* alkali metal bis(trimethylsilyl)amides $[MN(SiMe_3)_2]$ (**1**: M = Li, Na, and K) (Fig. 1 shows the structure of complexes **1–8**).[9] The heavier group 2 catalysts, **2** and **3**, were tested by Hill and Barrett. The homoleptic alkaline earth (Ca, Sr and Ba) amides **2** displayed higher activity than β-the diketiminato calcium complex **3**.[10] The triamidoamine-supported zirconium complex **4** showed moderate activity for the CPPC reaction.[11] In the attempt to test the rare-earth metals, the half-sandwich lanthanum aminobenzyl complex **5-La** was found by Hou *et al.* to display the highest activity among the rare-earth metals because of its largest ionic

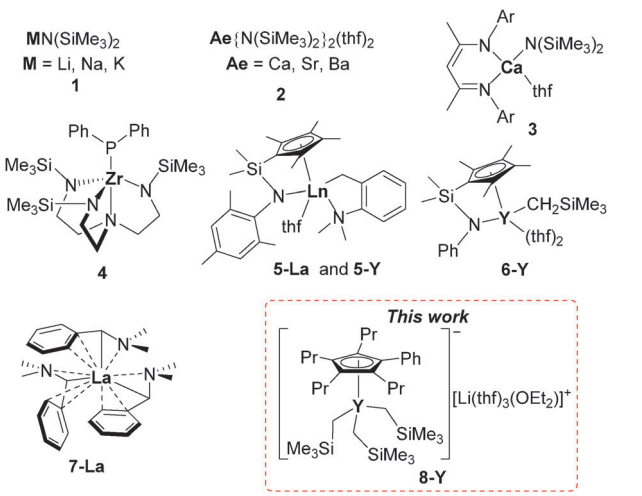


Fig. 1 The reported catalyst precursors for the CPPC reaction.

[a] *Beijing National Laboratory for Molecular Sciences, MOE Key Laboratory of Bioorganic Chemistry and Molecular Engineering, College of Chemistry, Peking University, Beijing 100871, China. E-mail: wx_zhang@pku.edu.cn*
[b] *State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin, 300071, China*

† Electronic supplementary information (ESI) available: The detailed experimental synthesis and characterization. CCDC 1047716 (**9i**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5nj01136a

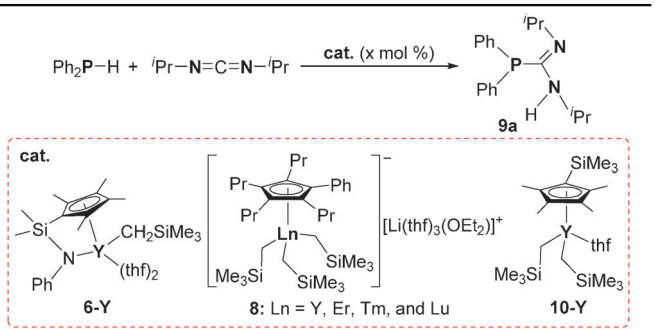
radius (1.032 Å for La^{3+}); however, the corresponding yttrium complexes **5-Y** and **6-Y** (0.900 Å for Y^{3+}) showed evidently lower activity.[12] Schmidt *et al.* reported the CPPC reaction using homoleptic α-metalated *N*,*N*-dimethylbenzylamine lanthanum complex **7-La**, in which three *N*,*N*-dimethylbenzylamine ligands were released *via* protonolysis with phosphines to yield the active La–P species.[13] All these reported catalyst systems involved only the neutral metal amides or alkyl complexes. We reported the synthesis and structural characterization of half-sandwich rare-earth metal tris(trimethylsilylmethyl) ate complexes bearing one 1-phenyl-2,3,4,5-tetrapropylcyclopentadienyl ligand and their catalytic application in CGAC reactions to construct guanidines.[14] We envision that these ate complexes, which might have the advantages of the neutral metal amides and alkyl complexes, could serve as good catalyst precursors for the CPPC reaction to construct phosphaguanidines. Herein, we report these results.

Results and discussion

Condition screening

As a control experiment, barely mixing diphenylphosphine and *N*,*N*′-diisopropylcarbodiimide (DIC) in the absence of catalysts resulted in no phosphaguanidine product, even at 140 °C for 24 h in C_6D_5Cl (Table 1, entry 1). However, when a small amount of **8-Y** was added, the corresponding phosphaguanidine **9a** can be detected by ^{31}P NMR (Table 1, entries 2–6). Both polar solvent (THF) and non-polar solvents (benzene and toluene) were tested, and it was revealed that THF was the best option probably owing to the excellent solubility for the rare-earth complex (Table 1, entries 2–4). Low yields were found when the reaction was carried out at room temperature (Table 1, entry 5) or under low catalyst loading (1 mol%) (Table 1, entry 6). All of these complexes with different metal centers (Er, Tm and Lu) had catalytic activities (Table 1, entries 7–9). The ate complex **8-Y** showed better catalytic activity than the neutral yttrium complexes such as the half-sandwich constrained-geometry complex **6-Y**, mono-Cp complex **10-Y**, and tris(trimethylsilylmethyl) complex $Y(CH_2TMS)_3(THF)_2$. The comparison clearly shows the significance of combining cyclopentadiene-based ligands and ate complexes (Table 1, entries 4 and 11–13).

Table 1 Condition screening[a]



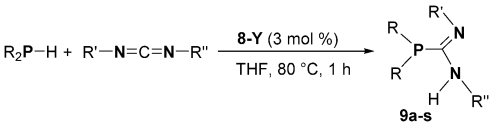
Entry	Cat. (mol%)	Solvent	Temp. (°C)	Time (h)	Yield[b] (%)
1	0	C_6D_5Cl	140	24	0
2	**8-Y** (3)	C_6D_6	80	7	78
3	**8-Y** (3)	Tol-d_8	80	7	67
4	**8-Y** (3)	THF-d_8	80	1	97
5	**8-Y** (3)	THF-d_8	r.t.	1	35
6	**8-Y** (1)	THF-d_8	80	1	45
7	**8-Er** (3)	THF-d_8	80	1	52
8	**8-Tm** (3)	THF-d_8	80	1	68
9	**8-Lu** (3)	THF-d_8	80	1	49
10	**8-Y** (5)	THF-d_8	r.t.	12	62
11	**6-Y** (3)	THF-d_8	80	1	86
12	**10-Y** (3)	THF-d_8	80	8	65
13	$Y(CH_2TMS)_3(THF)_2$	THF-d_8	80	3	66

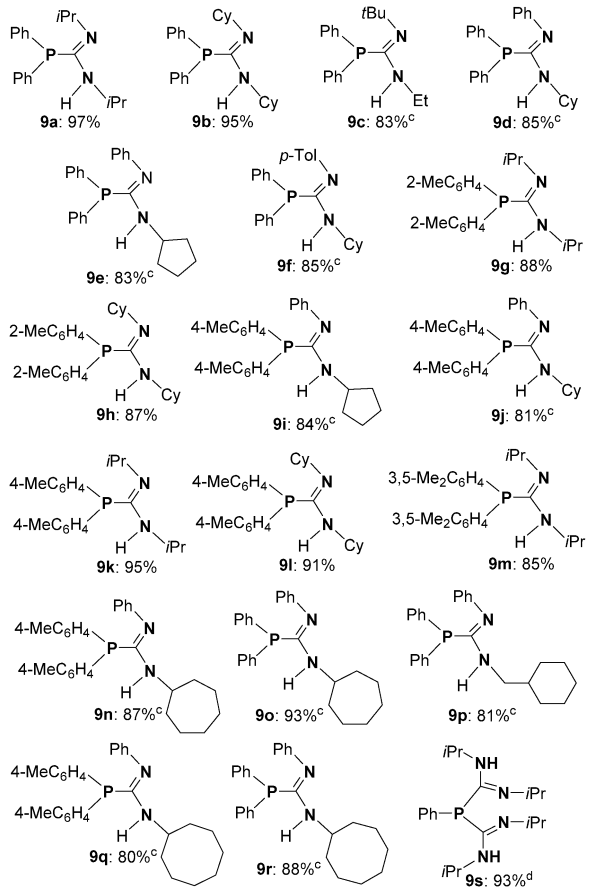
[a] Conditions: diphenylphosphine, 0.23 mmol; *N*,*N*′-diisopropylcarbodiimide, 0.20 mmol. [b] Determined by ^{31}P NMR.

Substrate scope

The anionic rare-earth complex **8-Y** was chosen for the CPPC reaction, and representative results are summarized in Table 2. Various carbodiimides could be applied to the present conditions. When symmetric *N*,*N*′-dialkylcarbodiimides such as DIC and *N*,*N*′-dicyclohexylcarbodiimide (DCC) were utilized, the

Table 2 Substrate scope[a,b]





[a] Conditions: phosphine, 0.53 mmol; carbodiimide, 0.50 mmol, THF, 5 mL, unless otherwise noted. [b] Isolated yield. [c] 6 mol% catalyst, 24 h. [d] Carbodiimide, 1 mmol.

corresponding phosphaguanidines (**9a**, **9b**, **9g**, **9h**, and **9k–m**) were obtained in excellent yields under the relatively mild conditions. In the case of *N*-ethyl-*N*′-*tert*-butylcarbodiimides (**9c**), this CPPC reaction need higher catalyst loadings and long reaction time probably due to the steric hindrance of the *tert*-butyl group. Unsymmetric *N*-aryl-*N*′-alkyl carbodiimides, such as *N*-phenyl-*N*′-cyclopentyl, *N*-phenyl-*N*′-cyclohexyl, *N*-*p*-tol-*N*′-cyclohexyl, *N*-phenyl-*N*′-cycloheptyl, *N*-phenyl-*N*′-cyclooctyl and *N*-phenyl-*N*′-CH_2-cyclohexyl carbodiimides, could also be applied to construct phosphaguanidines (**9d–f**, **9i**, **9j** and **9n–r**), but higher catalyst loadings and long reaction time were required owing to the low electrophilicity of *N*-alky-*N*′-aryl carbodiimides for accepting nucleophilic attack of the phosphine. The phosphaguanylation products originating from bulky carbodiimides such as *N*,*N*′-bis(2,6-diisopropylphenyl)carbodiimide and diphenylphosphine, were not observed probably owing to the steric hindrance at the nitrogen atom, which prevents the coordination of the carbodiimide to the rare-earth metal center. Most diarylphosphines could be utilized in this reaction to afford the corresponding products (**9a–r**) in good yields. The dialkylphosphines such as di-iso-butylphosphine could not be applied probably due to the decreased acidity compared to diarylphosphines. When the primary phosphine $PhPH_2$ was treated with one equivalent of DIC, both mono- and double-addition products iPrN═C(PHPh)(NHiPr), $PhP\{iPrN{=}C(NHiPr)\}_2$ could be detected by ^{31}P NMR (mono-addition product: −62.1 ppm and double-addition product: −34.9 ppm). When the amount of DIC was increased to 2 equivalents, the double-addition product **9s** can be obtained exclusively in 93% yield.

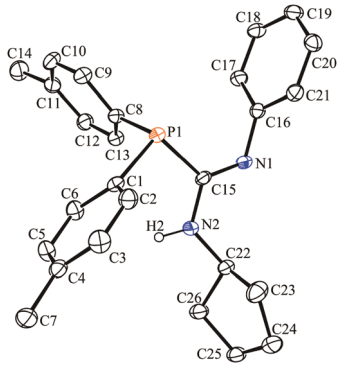


Fig. 2 ORTEP drawing of **9i** with 30% ellipsoids. Hydrogen atoms, except that on nitrogen atom N2, are omitted for clarity.

Although phosphaguanidines could, in principle, have eight possible isomers, E_{syn}-(α,β), E_{anti}-(α,β), Z_{syn}-(α,β), and Z_{anti}-(α,β),[15] all of the ^1H, ^{13}C and ^{31}P NMR spectra of **9a–r** indicated only one isomer in solution. X-ray single crystal diffraction analysis of phosphaguanidine **9i** reveals it is an E_{syn}-(α) isomer with the phenyl group placed on the C═N double bond in the solid state (Fig. 2).

To gain further insight into the mechanism of the CPPC reaction, we conducted a stoichiometric reaction by *in situ* NMR monitoring. The original spectra of **8-Y** in THF-d_8 without TMS internal standard is illustrated in Fig. 3a. The double peaks of

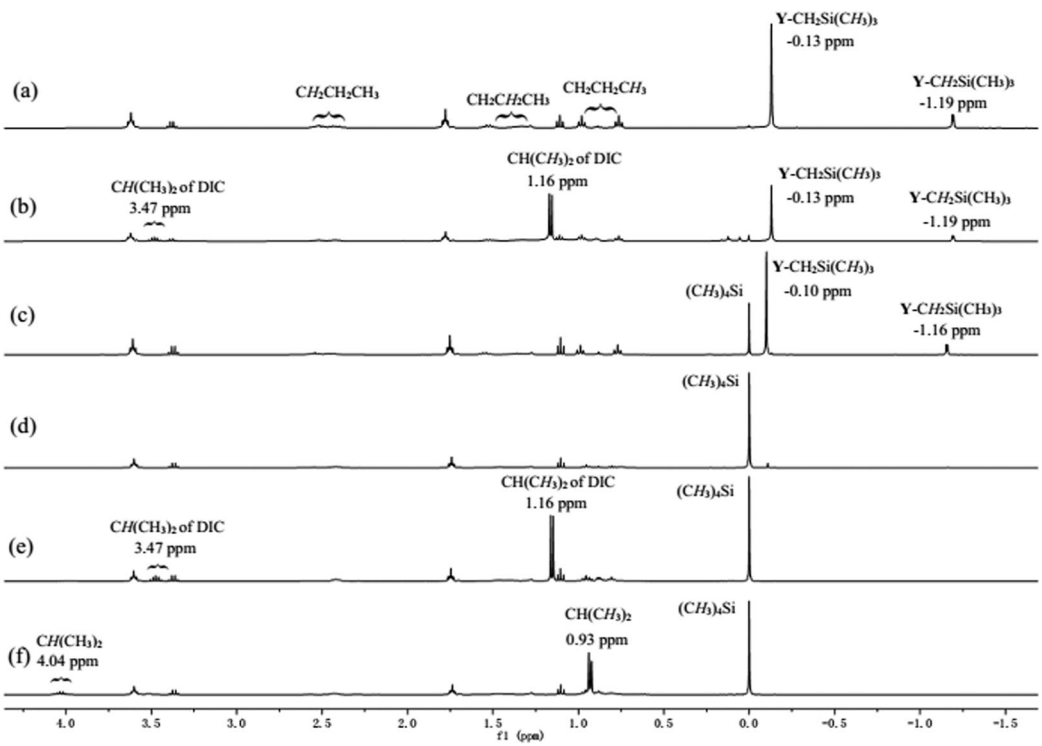
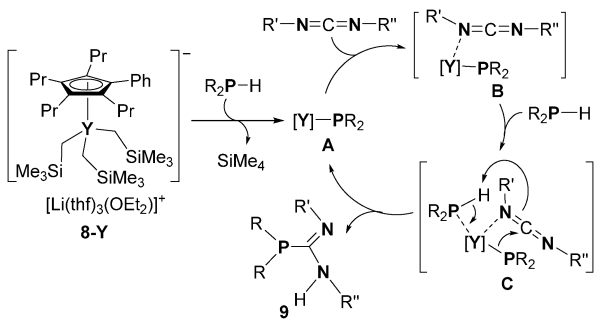


Fig. 3 *In situ* NMR spectra of stoichiometric reaction. (a) **8-Y**; (b) **8-Y** + 3DIC at room temperature for 12 h; (c) **8-Y** + $3Ph_2PH$ at room temperature for 12 h; (d) **8-Y** + $3Ph_2PH$ at room temperature for 24 h; (e) **8-Y** + $3Ph_2PH$ + 3DIC at 80 °C for 1 h; (f) (**8-Y** + $3Ph_2PH$ + 3DIC) + $3Ph_2PH$ at room temperature for 15 min.

−1.19 ppm and single peak of −0.13 ppm were ascribed to CH_2 and CH_3 of CH_2SiMe_3, respectively. When **8-Y** was treated with 3 equivalents of DIC, the ^{1}H NMR spectra showed the peaks of DIC remained unchanged after 12 h at room temperature (Fig. 3b). This result shows that the insertion of DIC into the Y–CH_2SiMe_3 alkyl bond does not occur at room temperature. However, when **8-Y** was treated with 3 equivalents of Ph_2PH, the reaction mixture turned light yellow immediately. After 12 h at room temperature, the ^{1}H NMR spectra showed that the integral of the CH_2SiMe_3 groups decreased and the peak of $SiMe_4$ was observed at 0 ppm (Fig. 3c). After 24 h at room temperature, the ^{1}H NMR spectra showed that the peaks of CH_2SiMe_3 almost disappeared (Fig. 3d). The formation of $SiMe_4$ resulted from the acid–base reaction between the phosphine P–H bond and Y–CH_2SiMe_3 alkyl bond. The comparative results show that the acid–base reaction between the P–H bond and Y–CH_2SiMe_3 alkyl bond is faster than the insertion of the carbodiimide into the Y–CH_2SiMe_3 alkyl bond at room temperature. This result also indicated that all of the three CH_2SiMe_3 groups in **8-Y** were involved in the acid–base reaction. Subsequent addition of 3 equivalents of DIC led apparently to the doublet peak at 1.16 ppm and multiplet peak at 3.47 ppm for CH_3 and CH of DIC in the ^{1}H NMR spectrum, respectively (Fig. 3e). After heating this mixture at 80 °C for 1 h, no evident change in ^{1}H NMR spectrum was observed, which indicated that DIC did not insert into the Y–P bond. Interestingly, when another 3 equivalents of Ph_2PH were added into the abovementioned solution, all the peaks belonging to the iPr moiety of DIC changed within 15 min (Fig. 3f). The peaks of CH_3 and CH of DIC shifted to 0.93 ppm and 4.04 ppm, which were consistent with the corresponding chemical shifts of the iPr of phosphaguanidine **9a**. After the addition of an excess of Ph_2PH and DIC in 1 : 1 ratio, the catalytic formation of phosphaguanidine **9a** was evidently observed.

A possible reaction mechanism for the CPPC reaction was proposed and is shown in Scheme 1. The formation of the active phosphide species **A** might undergo two possible pathways: (i) the acid–base reaction between a phosphine and **8-Y**, and (ii) the insertion of the carbodiimide into the Y-alkyl bond followed by protonolysis yielding an amidine and Y-phosphido complex **A**. The insertion pathway can be excluded, because the acid–base reaction is faster than the insertion reaction, according to the experimental results shown in Fig. 3b and c. The coordination of carbodiimides took place to form the coordinate species **B**.



Scheme 1 A plausible mechanism for the CPPC reaction.

The fast coordination and disassociation of DIC to the yttrium center in THF was probably out of the NMR time scale, so the evident chemical shifts of DIC were not observed, which was consistent with the observation of Fig. 3e. Then, the coordination of phosphine might yield the adduct **C**. The intramolecular nucleophilic attack of the Y–P bond on the central carbon of the coordinate carbodiimide and the protonolysis with the R_2P–H bond released the phosphaguanidine product **9** and regenerated **A** to finish the catalytic cycle.

Conclusions

In summary, we have reported a half-sandwich yttrium tris(trimethylsilylmethyl) ate complex catalyzed phosphaguanylation reaction of phosphines with carbodiimides to efficiently prepare phosphaguanidines. The present yttrium catalyst system is easier to prepare and cheaper than those reported using neutral lanthanum complexes. It displays the best catalytic activity among the known yttrium complexes probably owing to the cooperative effect between the anionic yttrium core and cationic lithium moiety. Further investigation on the mechanism and catalytic application is underway.

Experimental section

General considerations

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. All reactions were conducted under a slightly positive pressure of dry nitrogen using standard Schlenk line techniques or under a nitrogen atmosphere in a Vigor (SG 1200/750TS-F) glovebox. The nitrogen in the glove box was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer to ensure both were always below 1 ppm. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvents were purified by an Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in the glovebox. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of J. Young valve NMR tubes (Wilmad 528-JY). ^{1}H, ^{13}C NMR and ^{31}P spectra were recorded using Bruker-400 spectrometer (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C and 160 MHz for ^{31}P) at room temperature. High-resolution mass spectra (HRMS) were recorded with a Bruker Apex IV FTMS mass spectrometer using an ESI (electrospray ionization) source.

NMR tube reaction

In a glovebox, a J. Young valve NMR tube was charged with **8-Y** (5.7 mg, 0.006 mmol), THF (0.5 mL), diphenylphosphine (43 mg, 0.23 mmol), and *N*,*N*′-diisopropylcarbodiimide (25 mg, 0.20 mmol). The tube was taken out of the glovebox and then heated at 80 °C in an oil bath for 1 h. The formation of the phosphaguanidine was monitored by ^{31}P NMR spectroscopy.

Preparative scale reaction

In a glovebox, the mixture of a THF solution (1 mL) of **8-Y** (14.4 mg, 0.015 mmol) and a THF solution (2 mL) of diphenylphosphine (99 mg, 0.53 mmol) was added to a Schlenk tube. Then, *N*,*N*′-diisopropylcarbodiimide (63 mg, 0.5 mmol) was added to the abovementioned reaction mixture. The Schlenk tube was taken outside the glovebox, and the mixture was stirred at 80 °C for 1 h. After the stirring, the solvent was removed under reduced pressure. The residue was extracted with hexane and filtered to give a clean solution. After the removal of the solvent under vacuum, the residue was recrystallized in hexane to provide the phosphaguanidine **9a**. Compounds **9b–s** were prepared in a similar procedure.

iPrN═C(PPh$_2$)(NHiPr) (9a)[9]. Colorless solid, isolated yield 97% (151 mg); ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 0.96 (d, J = 6.4 Hz, 6H; CH(CH_3)$_2$), 1.26 (d, J = 6.1 Hz, 6H; CH(CH_3)$_2$), 3.66 (d, ^3J = 6.3 Hz, 1H; NH), 4.29–4.47 (m, 2H; CH), 7.01–7.08 (m, 6H; C_6H_5), 7.44–7.49 (m, 4H; C_6H_5) ppm; ^{1}H NMR (400 MHz, THF-d_8, Me_4Si): δ = 0.92 (d, J = 2.7 Hz, 6H; CH(CH_3)$_2$), 0.94 (d, J = 3.0 Hz, 6H; CH(CH_3)$_2$), 3.52 (d, ^3J = 6.4 Hz, 1H; NH), 3.98–4.08 (m, 2H; CH), 7.34–7.40 (m, 10H; C_6H_5) ppm.

CyN═C(PPh$_2$)(NHCy) (9b)[9]. Colorless solid, isolated yield 95% (186 mg); ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 0.95–1.92 (m, 20H; Cy), 3.82 (d, ^3J = 6.8 Hz, 1H; NH), 4.07–4.19 (m, 2H; CH), 7.02–7.09 (m, 6H; C_6H_5), 7.49–7.52 (m, 4H; C_6H_5) ppm.

***t*BuN═C(PPh$_2$)(NHEt) (9c)[9].** Colorless solid, isolated yield 83% (130 mg); ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 1.31 (t, J = 7.2 Hz, 3H; CH_2CH_3), 1.36 (s, 9H; C(CH_3)$_3$), 3.77–3.83 (m, 3H, NH and CH_2CH_3), 7.01–7.06 (m, 6H; C_6H_5), 7.45–7.49 (m, 4H; C_6H_5) ppm.

PhN═C(PPh$_2$)(NHCy) (9d)[9]. Colorless solid, isolated yield 85% (164 mg); ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 0.88–1.94 (m, 10H; Cy), 4.22–4.24 (m, 1H; CH), 4.38 (d, ^3J = 7.0 Hz, 1H; NH), 6.84 (t, J = 7.6 Hz, 1H; C_6H_5), 7.03–7.11 (m, 10H; C_6H_5), 7.44 (t, J = 6.3 Hz, 4H; C_6H_5) ppm.

PhN═C(PPh$_2$){NH–(CH$_2$)$_5$} (9e). Colorless solid, isolated yield 83% (155 mg); ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 1.23–1.87 (m, 8H; –(CH_2)$_4$–), 4.38 (d, ^3J = 6.3 Hz, 1H; NH), 4.55–4.61 (m, 1H; CH), 6.83–6.87 (m, 1H; C_6H_5), 7.00–7.12 (m, 10H; C_6H_5), 7.38–7.43 (m, 4H; C_6H_5) ppm; ^{13}C NMR (100 MHz, C_6D_6, Me_4Si): δ = 23.8, 33.2, 53.9, 122.3, 123.3 (d, $^4J_{pc}$ = 1.8 Hz), 128.6, 128.9 (d, $^3J_{pc}$ = 6.8 Hz), 129.4, 134.4 (d, $^2J_{pc}$ = 20.1 Hz), 135.3 (d, $^1J_{pc}$ = 15.5 Hz), 151.9 (d, $^3J_{pc}$ = 12.1 Hz), 156.8 (d, $^1J_{pc}$ = 36.7 Hz) ppm; ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ = −14.6 ppm; HRMS: *m*/*z* calcd for $C_{24}H_{26}N_2P$: 373.1828 [M + H]$^+$; found: 373.1817.

***p*-tolN═C(PPh$_2$)(NHCy) (9f).** Colorless solid, isolated yield 85% (170 mg); ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 0.96–1.95 (m, 10H; Cy), 2.07 (s, 3H; Me), 4.25–4.26 (m, 1H; CH), 4.35 (d, ^3J = 6.6 Hz, 1H; NH), 6.89–7.05 (m, 10H; C_6H_5), 7.43–7.45 (m, 4H; C_6H_4) ppm; ^{13}C NMR (100 MHz, C_6D_6, Me_4Si): δ = 20.9, 24.6, 26.0, 32.6, 49.8, 123.1 (d, $^4J_{pc}$ = 1.6 Hz), 128.9 (d, $^3J_{pc}$ = 6.8 Hz), 129.2, 129.4, 131.1, 134.4 (d, $^2J_{pc}$ = 20.0 Hz), 135.5 (d, $^1J_{pc}$ = 15.8 Hz), 149.4 (d, $^3J_{pc}$ = 12.5 Hz), 156.1 (d, $^1J_{pc}$ = 36.3 Hz) ppm; ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ = −14.9 ppm; HRMS: *m*/*z* calcd for $C_{26}H_{30}N_2P$: 401.2141 [M + H]$^+$; found: 401.2144.

iPrN═C{P(C$_6$H$_4$Me-2)$_2$}(NHiPr) (9g)[9]. Colorless solid, isolated yield 88% (150 mg); ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 0.94 (d, J = 6.4 Hz, 6H; CH(CH_3)$_2$), 1.33 (d, J = 5.4 Hz, 6H; CH(CH_3)$_2$), 2.41 (s, 6H; Me), 3.72 (d, ^3J = 6.4 Hz, 1H; NH), 4.34–4.47 (m, 2H; CH), 6.92–7.06 (m, 8H; C_6H_4) ppm.

CyN═C{P(C$_6$H$_4$Me-2)$_2$}(NHCy) (9h). Colorless solid, isolated yield 87% (183 mg); ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 0.89–1.94 (m, 20H; Cy), 2.45 (s, 6H; Me), 3.90 (d, ^3J = 7.0 Hz, 1H; NH), 4.08–4.26 (m, 2H, CH), 6.98–7.07 (m, 8H; C_6H_4) ppm; ^{13}C NMR (100 MHz, C_6D_6, Me_4Si): δ = 21.3 (d, $^3J_{pc}$ = 21.7 Hz), 24.7, 25.3, 26.1, 26.4, 32.7, 35.9, 49.1, 60.9 (d, $^3J_{pc}$ = 35.2 Hz), 126.8, 129.6, 130.6 (d, $^3J_{pc}$ = 4.5 Hz), 143.0 (d, $^2J_{pc}$ = 25.9 Hz), 151.8 (d, $^1J_{pc}$ = 30.2 Hz) ppm; ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ = −32.9 ppm; HRMS: *m*/*z* calcd for $C_{27}H_{38}N_2P$: 421.2767 [M + H]$^+$; found: 421.2754.

PhN═C{P(C$_6$H$_4$Me-4)$_2$}{NH–(CH$_2$)$_5$} (9i). Colorless solid, isolated yield 84% (168 mg); ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 1.28–1.90 (m, 8H; –(CH_2)$_4$–), 1.98 (s, 6H; Me), 4.52 (d, ^3J = 6.4 Hz, 1H; NH), 4.61–4.65 (m, 1H; CH), 6.84–6.86 (m, 1H; C_6H_5), 6.89 (d, J = 7.6 Hz, 4H; C_6H_4), 7.12 (d, J = 4.7 Hz, 4H; C_6H_5), 7.39 (t, J = 7.6 Hz, 4H; C_6H_4) ppm; ^{13}C NMR (100 MHz, C_6D_6, Me_4Si): δ = 21.1, 23.8, 33.3, 53.8, 122.2, 123.3 (d, $^4J_{pc}$ = 1.8 Hz), 128.5, 129.8 (d, $^3J_{pc}$ = 7.0 Hz), 132.1 (d, $^1J_{pc}$ = 14.3 Hz), 134.5 (d, $^2J_{pc}$ = 20.3 Hz), 139.4, 152.1 (d, $^3J_{pc}$ = 11.9 Hz), 157.4 (d, $^1J_{pc}$ = 37.1 Hz) ppm; ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ = −16.2 ppm; HRMS: *m*/*z* calcd for $C_{26}H_{30}N_2P$: 401.2141 [M + H]$^+$; found: 401.2129. Single crystals of **9i** suitable for X-ray analysis were grown in THF–hexane for 1 day at room temperature.

PhN═C{P(C$_6$H$_4$Me-4)$_2$}(NHCy) (9j). Colorless solid, isolated yield 81% (168 mg); ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 0.88–1.42 (m, 10H; Cy), 2.00 (s, 6H; Me), 4.26–4.30 (m, 1H; CH), 4.50 (d, ^3J = 7.2 Hz, 1H; NH), 6.83–6.88(m, 1H; C_6H_5), 6.91 (d, J = 7.6 Hz, 4H; C_6H_4), 7.12 (d, J = 4.5 Hz, 4H; C_6H_5), 7.42 (t, J = 7.6 Hz, 4H; C_6H_4) ppm; ^{13}C NMR (100 MHz, C_6D_6, Me_4Si): δ = 21.1, 24.8, 26.0, 32.7, 49.9, 122.1, 123.4 (d, $^4J_{pc}$ = 1.7 Hz), 128.5, 129.8 (d, $^3J_{pc}$ = 7.1 Hz), 132.1 (d, $^1J_{pc}$ = 14.4 Hz), 134.5 (d, $^2J_{pc}$ = 20.3 Hz), 139.4, 152.1 (d, $^3J_{pc}$ = 12.0 Hz), 156.8 (d, $^1J_{pc}$ = 36.7 Hz) ppm; ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ = −15.9 ppm; HRMS: *m*/*z* calcd for $C_{27}H_{32}N_2P$: 415.2298 [M + H]$^+$; found: 415.2287.

iPrN═C{P(C$_6$H$_4$Me-4)$_2$}(NHiPr) (9k)[9]. Colorless solid, isolated yield 95% (162 mg); ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 1.00 (d, J = 6.4 Hz, 6H; CH(CH_3)$_2$), 1.28 (d, J = 6.1 Hz, 6H; CH(CH_3)$_2$), 2.02 (s, 6H; Me), 3.79 (d, ^3J = 6.6 Hz, 1H; NH), 4.34–4.51 (m, 2H; CH), 6.93 (d, J = 7.5 Hz, 4H; C_6H_4), 7.44 (t, J = 7.7 Hz, 4H; C_6H_4) ppm.

CyN═C{P(C$_6$H$_4$Me-4)$_2$}(NHCy) (9l). Colorless solid, isolated yield 91% (191 mg); ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 0.93–1.98 (m, 20H; Cy), 2.02 (s, 6H; Me), 3.94 (d, ^3J = 7.0 Hz, 1H; NH), 4.13–4.24 (m, 2H; CH), 6.96 (d, J = 7.6 Hz, 4H; C_6H_4), 7.49 (t, J = 7.6 Hz, 4H; C_6H_4) ppm; ^{13}C NMR (100 MHz, C_6D_6, Me_4Si): δ = 21.1, 24.7, 25.3, 26.2, 26.4, 32.7, 35.8, 49.2, 60.2 (d, $^3J_{pc}$ = 33.6 Hz), 129.8 (d, $^3J_{pc}$ = 7.0 Hz), 132.5 (d, $^1J_{pc}$ = 13.2 Hz), 134.4 (d, $^2J_{pc}$ = 19.7 Hz), 139.2, 152.8 (d, $^1J_{pc}$ = 31.8 Hz) ppm; ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ = −19.5 ppm; HRMS: *m*/*z* calcd for $C_{27}H_{38}N_2P$: 421.2767 [M + H]$^+$; found: 421.2760.

iPrN═C{P($C_6H_3Me_2$-3,5)$_2$}{NHiPr) (9m)[9]. Colorless solid, isolated yield 85% (157 mg); ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 1.03 (d, J = 6.4 Hz, 6H; CH(CH_3)$_2$), 1.32 (d, J = 6.1 Hz, 6H; CH(CH_3)$_2$), 2.03 (s, 12H; Me), 3.91 (d, ^3J = 6.6 Hz, 1H; NH), 4.37–4.54 (m, 2H, CH), 6.75 (s, 2H; C_6H_3), 7.28 (d, J = 8.0 Hz, 4H; C_6H_3) ppm.

PhN═C{P(C_6H_4Me-4)$_2$}{NH–(CH$_2$)$_7$} (9n). Colorless solid, isolated yield 87% (186 mg); ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 1.23–1.97 (m, 12H; –(CH_2)$_6$–), 2.01 (s, 6H; Me), 4.44–4.45 (m, 1H; CH), 4.55 (d, ^3J = 7.2 Hz, 1H; NH), 6.82–6.86 (m, 1H; C_6H_5), 6.92 (d, J = 7.7 Hz, 4H; C_6H_4),7.09 (d, J = 4.6 Hz, 4H; C_6H_5), 7.41 (t, J = 7.7 Hz, 4H; C_6H_4) ppm; ^{13}C NMR (100 MHz, C_6D_6, Me_4Si): δ = 21.1, 24.3, 28.1, 34.5, 52.1, 122.0, 123.3 (d, $^4J_{pc}$ = 1.7 Hz), 128.4, 129.8 (d, $^3J_{pc}$ = 7.0 Hz), 132.0 (d, $^1J_{pc}$ = 14.3 Hz), 134.4 (d, $^2J_{pc}$ = 20.3 Hz), 139.4, 152.1 (d, $^3J_{pc}$ = 12.0 Hz), 156.6 (d, $^1J_{pc}$ = 36.7 Hz) ppm; ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ = −15.9 ppm; HRMS: m/z calcd for $C_{28}H_{34}N_2P$: 429.2454 [M + H]$^+$; found: 429.2444.

PhN═C(PPh$_2$){NH–(CH$_2$)$_7$} (9o). Colorless solid, isolated yield 93% (186 mg); ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 1.21–1.90 (m, 12H; –(CH_2)$_6$–), 4.43 (br, 2H; CH and NH), 6.82–6.86 (m, 1H; C_6H_5), 7.03–7.10 (m, 10H; C_6H_5), 7.42–7.45 (m, 4H; C_6H_5) ppm; ^{13}C NMR (100 MHz, C_6D_6, Me_4Si): δ = 24.2, 28.1, 34.4, 52.1, 122.2, 123.3 (d, $^4J_{pc}$ = 1.7 Hz), 128.5, 128.9 (d, $^3J_{pc}$ = 6.9 Hz), 129.4, 134.4 (d, $^2J_{pc}$ = 20.1 Hz), 135.2 (d, $^1J_{pc}$ = 15.6 Hz), 151.9 (d, $^3J_{pc}$ = 12.2 Hz), 156.1 (d, $^1J_{pc}$ = 36.9 Hz) ppm; ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ = −14.3 ppm; HRMS: m/z calcd for $C_{26}H_{30}N_2P$: 401.2141 [M + H]$^+$; found: 401.2131.

PhN═C(PPh$_2$)(NHCH$_2$Cy) (9p). Colorless solid, isolated yield 81% (162 mg); ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 0.65–1.58 (m, 11H; Cy), 3.31 (t, J = 5.8 Hz, 2H; CH_2), 4.46 (t, J = 5.0 Hz, 1H; NH), 6.81–6.85 (m, 1H; C_6H_5), 7.03–7.10 (m, 10H; C_6H_5), 7.40–7.44 (m, 4H; C_6H_5) ppm; ^{13}C NMR (100 MHz, C_6D_6, Me_4Si): δ = 26.1, 26.7, 30.9, 37.6, 48.5, 122.1, 123.2 (d, $^4J_{pc}$ = 1.6 Hz), 128.5, 128.9 (d, $^3J_{pc}$ = 6.8 Hz), 129.4, 134.4 (d, $^2J_{pc}$ = 20.1 Hz), 135.0 (d, $^1J_{pc}$ = 15.4 Hz), 151.9 (d, $^3J_{pc}$ = 11.9 Hz), 157.3 (d, $^1J_{pc}$ = 36.2 Hz) ppm; ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ = −13.5 ppm; HRMS: m/z calcd for $C_{26}H_{30}N_2P$: 401.2141 [M + H]$^+$; found: 401.2141.

PhN═C{P(C_6H_4Me-4)$_2$}{NH–(CH$_2$)$_8$} (9q). Colorless solid, isolated yield 80% (177 mg); ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 1.30–1.92 (m, 14H; –(CH_2)$_7$–), 2.00 (s, 6H; Me), 4.45 (br, 1H; CH), 4.56 (d, ^3J = 7.1 Hz, 1H; NH), 6.82–6.87 (m, 1H; C_6H_5), 6.92 (d, J = 7.6 Hz, 4H; C_6H_4), 7.10 (d, J = 4.4 Hz, 4H; C_6H_5), 7.42 (t, J = 7.6 Hz, 4H; C_6H_4) ppm; ^{13}C NMR (100 MHz, C_6D_6, Me_4Si): δ = 21.1, 23.9, 25.7, 27.4, 32.1, 51.2, 122.1, 123.4 (d, $^4J_{pc}$ = 1.5 Hz), 128.5, 129.8 (d, $^3J_{pc}$ = 7.0 Hz), 132.1 (d, $^1J_{pc}$ = 14.4 Hz), 134.4 (d, $^2J_{pc}$ = 20.3 Hz), 139.4, 152.1 (d, $^3J_{pc}$ = 12.0 Hz), 156.5 (d, $^1J_{pc}$ = 36.9 Hz) ppm; ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ = −15.9 ppm; HRMS: m/z calcd for $C_{29}H_{36}N_2P$: 443.2611 [M + H]$^+$; found: 443.2602.

PhN═C(PPh$_2$){NH–(CH$_2$)$_8$} (9r). Colorless solid, isolated yield 88% (182 mg); ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 1.28–1.85 (m, 14H; –(CH_2)$_7$–), 4.44 (br, 2H; CH and NH), 6.82–6.86 (m, 1H; C_6H_5), 7.03–7.11 (m, 10H; C_6H_5), 7.42–7.45 (m, 4H; C_6H_5) ppm; ^{13}C NMR (100 MHz, C_6D_6, Me_4Si): δ = 23.8, 25.7, 27.5, 31.9, 51.2, 122.2, 123.3 (d, $^4J_{pc}$ = 1.2 Hz), 128.5, 128.9 (d, $^3J_{pc}$ = 6.8 Hz), 129.4, 134.4 (d, $^2J_{pc}$ = 20.1 Hz), 135.3 (d, $^1J_{pc}$ = 15.6 Hz), 151.9 (d, $^3J_{pc}$ = 12.2 Hz), 156.1 (d, $^1J_{pc}$ = 37.5 Hz) ppm; ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ = −14.3 ppm; HRMS: m/z calcd for $C_{27}H_{32}N_2P$: 415.2298 [M + H]$^+$; found: 415.2289.

PhP{iPrN═C(NHiPr)}$_2$ (9s). Colorless oil, isolated yield 93% (168 mg); ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 0.98 (d, J = 6.1 Hz, 6H; CH(CH_3)$_2$), 1.08 (d, J = 6.1 Hz, 6H; CH(CH_3)$_2$), 1.22 (d, J = 6.1 Hz, 6H; CH(CH_3)$_2$), 1.34 (d, J = 6.1 Hz, 6H; CH(CH_3)$_2$), 4.24–4.36 (m, 6H; CH and NH), 7.04–7.10 (m, 3H; C_6H_5), 7.51–7.55 (m, 2H; C_6H_5) ppm; ^{13}C NMR (100 MHz, C_6D_6, Me_4Si): δ = 22.4 (d, $^4J_{pc}$ = 2.9 Hz), 25.3 (d, $^4J_{pc}$ = 8.0 Hz), 42.9, 52.6 (d, $^3J_{pc}$ = 36.9 Hz), 129.2 (d, $^3J_{pc}$ = 6.4 Hz), 129.6, 133.3 (d, $^1J_{pc}$ = 17.6 Hz), 134.0 (d, $^2J_{pc}$ = 19.1 Hz), 151.4 (d, $^1J_{pc}$ = 35.4 Hz); ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ = −34.9 ppm; HRMS: m/z calcd for $C_{20}H_{36}N_4P$: 363.2672 [M + H]$^+$; found: 363.2669.

X-ray diffraction analysis

Data collections for **9i** were performed at 180 K with a SuperNova diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Using Olex2, the structure of **9i** was solved with the Superflip structure solution program using Charge Flipping and refined with the XL refinement package using Least Squares minimization. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number: CCDC 1047716.

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