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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

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

## Introduction

Catalytic guanylation reaction of amines with carbodiimides (CGAC reaction) has become a hot area because it provides a straightforward and atom-economical route to prepare guanidines (RN=C(NR′R″)NHR).[1-3] In contrast, 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 much 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), *i*Pr, 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 removing 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.

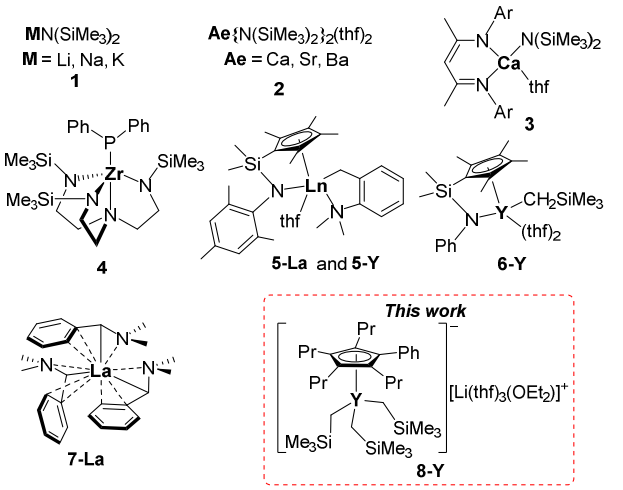


**Fig. 1** The reported catalyst precursors for the CPPC reaction

In 2006, Hou *et al.* reported the first CPPC reaction catalyzed via alkali metal bis(trimethylsilyl)amides $[MN(SiMe_3)_2]$ (**1**: M = Li, Na, K) (**Fig. 1** for 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*-diketiminato calcium complex **3**.[10] The triamidoamine-supported zirconium complex **4** showed the medium 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

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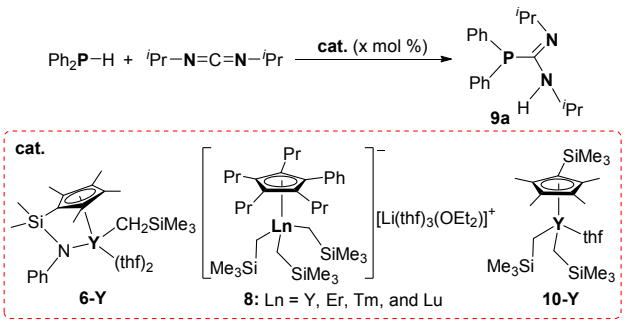
†*Electronic supplementary information (ESI) available: The detailed experimental synthesis and characterization. Compound* ***9i*** *CCDC: 1047716. For crystallographic data in CIF or other electronic format see DOI:*

Hou *et al*. to display the highest activity among the rare-earth metals because of the largest ionic radius (1.032 Å for $La^{3+}$), however, the corresponding yttrium complexes **5-Y** and **6-Y** (0.900 Å for $Y^{3+}$) showed the obviously 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 catalytic application in CGAC reaction to construct guanidines.[14] We envision that these ate complexes, which might have the potential advantages of the neutral metal amides and alkyl complexes, could serve as good catalyst precursors for the CPPC reaction to construct phosphaguanidines. Here we report these results.

**Table 1** Condition screening




| 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.

## Results and discussion

### Condition screening

As a control experiment, barely mixing of 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 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 the 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 the 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 combining significance of cyclopentadiene-based ligands and ate complex (Table 1, entries 4 and 11-13).

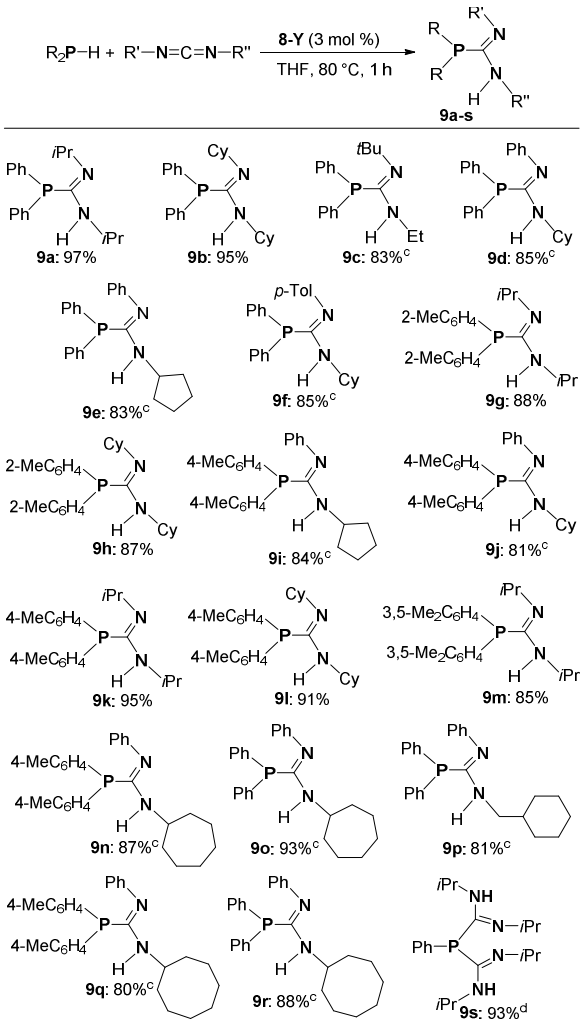
### Substrate scope

The anionic rare-earth complex **8-Y** was chosen for the CPPC reaction and representative results were summarized in Table 2. Various carbodiimides could be applied to the present conditions. When symmetric *N,N'*-dialkylcarbodiimides, such as DIC, *N,N'*-dicyclohexylcarbodiimide (DCC) were utilized, the corresponding phosphaguanidines (**9a**, **9b**, **9g**, **9h**, and **9k-m**) were obtained in excellent yields under the relatively milder conditions. In 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 *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 product originated from bulky carbodiimides such as *N,N'*-bis(2,6-diisopropylphenyl)carbodiimide and diphenylphosphine was not observed, probably owing to the steric hindrance at 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 dialkylphosphine, 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 *i*PrN=C(PHPh)(NH*i*Pr), PhP{*i*PrN=C(NH*i*Pr)}$_2$ could be detected by $^{31}P$ NMR (mono-addition product: -62.1 ppm 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.

Although phosphaguanidines could, in principle, have eight possible isomers $E_{syn}$-($\alpha$,$\beta$), $E_{anti}$-($\alpha$,$\beta$), $Z_{syn}$-($\alpha$,$\beta$), $Z_{anti}$-($\alpha$,$\beta$),[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 an $E_{syn}$-($\alpha$) isomer with the phenyl group placed on the C=N double bond in the solid state (**Fig. 2**).

**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.

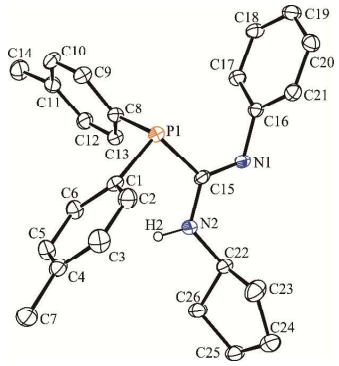



**Fig. 2** ORTEP drawing of **9i** with 30% ellipsoids. Hydrogen atoms, except that on nitrogen atom N2, are omitted for clarity.

To gain further insight into the mechanism of the CPPC reaction, we conducted the stoichiometric reaction by *in situ* NMR monitoring. The original spectra of **8-Y** in THF-$d_8$ without TMS internal standard was illustrated in **Fig. 3*a***. The double peaks of -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. 3*b***). 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 to 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 in 0 ppm (**Fig. 3*c***). And after 24 h at room temperature, the $^1$H NMR spectra showed that the peaks of $CH_2SiMe_3$ almost disappeared (**Fig. 3*d***). The formation of $SiMe_4$ resulted from the acid-base reaction between phosphine P–H bond and Y–$CH_2SiMe_3$ alkyl bond. The comparative results show that the acid-base reaction between 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 in 1.16 ppm and multiple peak in 3.47 ppm for $CH_3$ and CH of DIC in the $^1$H NMR spectrum, respectively (**Fig. 3*e***). After heating this mixture at 80 °C for 1 h, no obvious 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 above solution, all the peaks belonged to *i*Pr moiety of DIC changed within 15 min (**Fig. 3*f***). The peaks of $CH_3$ and CH of DIC shifted to 0.93 ppm and 4.04 ppm, which were in consistent with the corresponding chemical shifts of *i*Pr of phosphaguanidine **9a**. After an excess of $Ph_2PH$ and DIC in 1:1 ratio was added, the catalytic formation of phosphaguanidine **9a** was observed obviously.

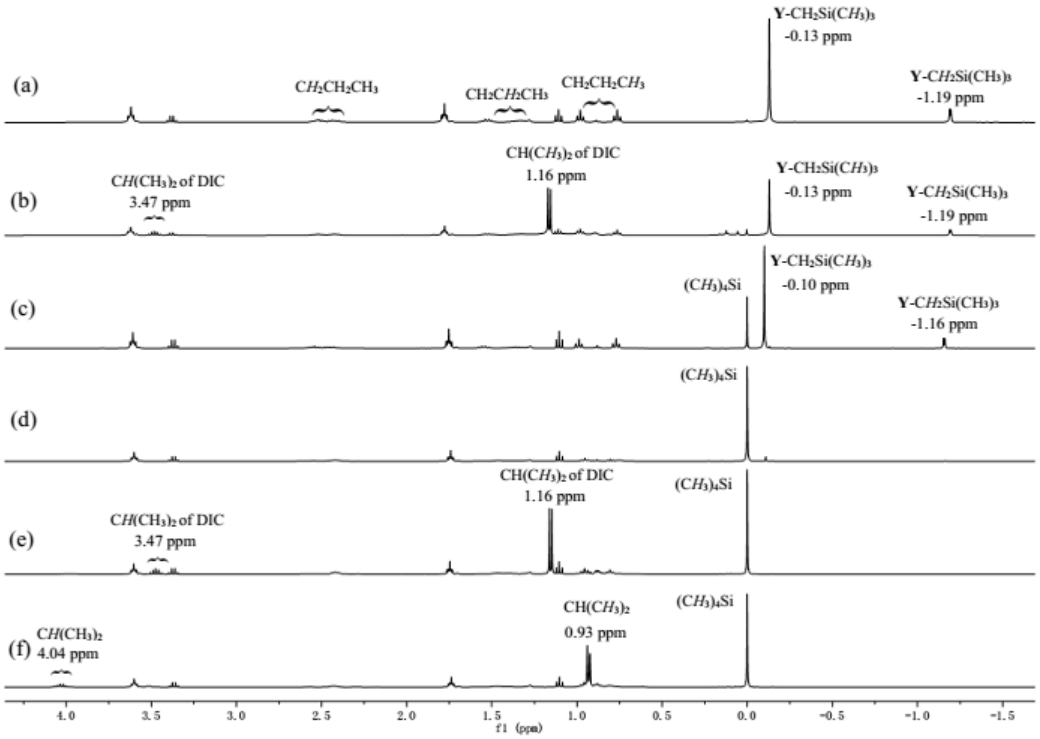
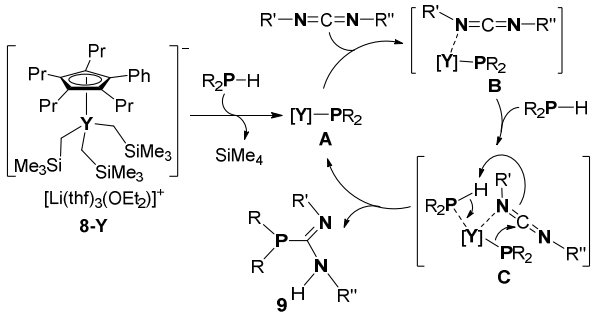



**Fig. 3** *In situ* NMR spectra of stoichiometric reaction. (a) **8-Y**; (b) **8-Y** + 3 DIC at room temperature for 12 h; (c) **8-Y** + 3 $Ph_2PH$ at room temperature for 12 h; (d) **8-Y** + 3 $Ph_2PH$ at room temperature for 24 h; (e) **8-Y** + 3 $Ph_2PH$ + 3 DIC at 80 °C for 1 h; (f) (**8-Y** + 3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




**Scheme 1** A plausible mechanism for the CPPC reaction.

A possible reaction mechanism for the CPPC reaction was proposed 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 as shown in **Fig. 3*b*** and **3*c***. The coordination of carbodiimides took place to form the coordinate species **B**. The fast coordination and disassociation of DIC to the yttrium center in THF was probably out of the NMR time scale, so the obvious chemical shifts of DIC were not observed, which was in consistent with the observation of **Fig. 3*e***. Then, the coordination of phosphine might yield the adduct **C**. The intramolecular nucleophilic attack of Y–P bond on the central carbon of the coordinate carbodiimide and the protonolysis with $R_2P$–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 prepare efficiently phosphaguanidines. The present yttrium catalyst system is easier to prepare and cheaper than those reported neutral lanthanum complexes. It displays the best catalytic activity among these 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 on Bruker-400 spectrometer (FT, 400 MHz for $^1$H; 100MHz for $^{13}$C and 160 MHz for $^{31}$P) at room temperature. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using 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. Formation of the phosphaguanidine was monitored by $^{31}$P NMR spectroscopy.

**Preparative scale reaction**

In a glovebox, the mixture of THF solution (1 mL) of **8-Y** (14.4 mg, 0.015 mmol) and 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 above 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 removal of the solvent under vacuum, the residue was recrystallized in hexane to provide the phosphaguanidine **9a**. Compounds **9b-m** were prepared in a similar procedure.

***i*PrN=C(PPh$_2$)(NH*i*Pr) (9a)**.[9] Colorless solid, isolated yield 97% (151 mg); $^1$H NMR (400 MHz, $C_6D_6$, $Me_4Si$): $\delta$ = 0.96 (d, $J$ = 6.4 Hz, 6H; CH(C$H_3$)$_2$), 1.26 (d, $J$ = 6.1 Hz, 6H; CH(C$H_3$)$_2$), 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-$d_8$, $Me_4Si$): $\delta$ = 0.92 (d, $J$ = 2.7 Hz, 6H; CH(C$H_3$)$_2$), 0.94 (d, $J$ = 3.0 Hz, 6H; CH(C$H_3$)$_2$), 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, $C_6D_6$, $Me_4Si$): $\delta$ = 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, $C_6D_6$, $Me_4Si$): $\delta$ = 1.31 (t, $J$ = 7.2 Hz, 3H; $CH_2CH_3$), 1.36 (s, 9H; C(C$H_3$)$_3$), 3.77-3.83 (m, 3H, NH and C$H_2$CH$_3$), 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, $C_6D_6$, $Me_4Si$): $\delta$ = 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, $C_6D_6$, $Me_4Si$): $\delta$ = 1.23-1.87 (m, 8H; -(C$H_2$)$_4$-), 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, $C_6D_6$,$Me_4Si$): $\delta$ = 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, $C_6D_6$): $\delta$ = -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, $C_6D_6$, $Me_4Si$): $\delta$ = 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, $C_6D_6$,$Me_4Si$): $\delta$ = 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, $C_6D_6$): $\delta$ = -14.9 ppm; HRMS: *m*/*z* calcd for $C_{26}H_{30}N_2P$: 401.2141 [M + H] $^+$; found: 401.2144.

***i*PrN=C{P(C$_6$H$_4$Me-2)$_2$}(NH*i*Pr) (9g)**.[9] Colorless solid, isolated yield 88% (150 mg); $^1$H NMR (400 MHz, $C_6D_6$, $Me_4Si$): $\delta$ = 0.94 (d, $J$ = 6.4 Hz, 6H; CH(C$H_3$)$_2$), 1.33 (d, $J$ = 5.4 Hz, 6H; CH(C$H_3$)$_2$), 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, $C_6D_6$, $Me_4Si$): $\delta$ = 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, $C_6D_6$,$Me_4Si$): $\delta$ = 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, $C_6D_6$): $\delta$ = -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, $C_6D_6$, $Me_4Si$): $\delta$ = 1.28-1.90 (m, 8H; -(C$H_2$)$_4$-), 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, $C_6D_6$,$Me_4Si$): $\delta$ = 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, $^{1}J_{pc}$ = 37.1 Hz) ppm; $^{31}P\{^{1}H\}$ NMR (160 MHz, $C_6D_6$): $\delta$ = -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, $C_6D_6$, $Me_4Si$): $\delta$ = 0.88-1.42 (m, 10H; Cy), 2.00 (s, 6H; Me), 4.26-4.30 (m, 1H; CH), 4.50 (d, $^{3}J$ = 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, $C_6D_6$,$Me_4Si$): $\delta$ = 21.1, 24.8, 26.0, 32.7, 49.9, 122.1, 123.4 (d, $^{4}J_{pc}$ = 1.7 Hz), 128.5, 129.8 (d, $^{3}J_{pc}$ = 7.1 Hz), 132.1 (d, $^{1}J_{pc}$ = 14.4 Hz), 134.5 (d, $^{2}J_{pc}$ = 20.3 Hz), 139.4, 152.1 (d, $^{3}J_{pc}$ = 12.0 Hz), 156.8 (d, $^{1}J_{pc}$ = 36.7 Hz) ppm; $^{31}P\{^{1}H\}$ NMR (160 MHz, $C_6D_6$): $\delta$ = -15.9 ppm; HRMS: *m/z* calcd for $C_{27}H_{32}N_2P$: 415.2298 [M + H] $^{+}$; found: 415.2287.

***i*PrN=C{P(C$_6$H$_4$Me-4)$_2$}(NH*i*Pr) (9k)**.[9] Colorless solid, isolated yield 95% (162 mg); $^{1}$H NMR (400 MHz, $C_6D_6$, $Me_4Si$): $\delta$ =1.00 (d, *J* = 6.4 Hz, 6H; CH(C$H_3$)$_2$), 1.28 (d, *J* = 6.1 Hz, 6H; CH(C$H_3$)$_2$), 2.02 (s, 6H; Me), 3.79 (d, $^{3}J$ = 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, $C_6D_6$, $Me_4Si$): $\delta$ = 0.93-1.98 (m, 20H; Cy), 2.02 (s, 6H; Me), 3.94 (d, $^{3}J$ = 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, $C_6D_6$,$Me_4Si$): $\delta$ = 21.1, 24.7, 25.3, 26.2, 26.4, 32.7, 35.8, 49.2, 60.2 (d, $^{3}J_{pc}$ = 33.6 Hz), 129.8 (d, $^{3}J_{pc}$ = 7.0 Hz), 132.5 (d, $^{1}J_{pc}$ = 13.2 Hz), 134.4 (d, $^{2}J_{pc}$ = 19.7 Hz), 139.2, 152.8 (d, $^{1}J_{pc}$ = 31.8 Hz) ppm; $^{31}P\{^{1}H\}$ NMR (160 MHz, $C_6D_6$): $\delta$ = -19.5 ppm; HRMS: *m/z* calcd for $C_{27}H_{38}N_2P$: 421.2767 [M + H] $^{+}$; found: 421.2760.

***i*PrN=C{P(C$_6$H$_3$Me$_2$-3,5)$_2$}(NH*i*Pr) (9m)**.[9] Colorless solid, isolated yield 85% (157 mg); $^{1}$H NMR (400 MHz, $C_6D_6$, $Me_4Si$): $\delta$ = 1.03 (d, *J* = 6.4 Hz, 6H; CH(C$H_3$)$_2$), 1.32 (d, *J* = 6.1 Hz, 6H; CH(C$H_3$)$_2$), 2.03 (s, 12H; Me), 3.91 (d, $^{3}J$ = 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$_6$H$_4$Me-4)$_2$}{NH-(CH$_2$)$_7$} (9n)**. Colorless solid, isolated yield 87% (186 mg); $^{1}$H NMR (400 MHz, $C_6D_6$, $Me_4Si$): $\delta$ = 1.23-1.97 (m, 12H; -(C$H_2$)$_6$-), 2.01 (s, 6H; Me), 4.44-4.45 (m, 1H; CH), 4.55 (d, $^{3}J$ = 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, $C_6D_6$,$Me_4Si$): $\delta$ = 21.1, 24.3, 28.1, 34.5, 52.1, 122.0, 123.3 (d, $^{4}J_{pc}$ = 1.7 Hz), 128.4, 129.8 (d, $^{3}J_{pc}$ = 7.0 Hz), 132.0 (d, $^{1}J_{pc}$ = 14.3 Hz), 134.4 (d, $^{2}J_{pc}$ = 20.3 Hz), 139.4, 152.1 (d, $^{3}J_{pc}$ = 12.0 Hz), 156.6 (d, $^{1}J_{pc}$ = 36.7 Hz) ppm; $^{31}P\{^{1}H\}$ NMR (160 MHz, $C_6D_6$): $\delta$ = -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, $C_6D_6$, $Me_4Si$): $\delta$ = 1.21-1.90 (m, 12H; -(C$H_2$)$_6$-), 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, $C_6D_6$,$Me_4Si$): $\delta$ = 24.2, 28.1, 34.4, 52.1, 122.2, 123.3 (d, $^{4}J_{pc}$ = 1.7 Hz), 128.5, 128.9 (d, $^{3}J_{pc}$ = 6.9 Hz), 129.4, 134.4 (d, $^{2}J_{pc}$ = 20.1 Hz), 135.2 (d, $^{1}J_{pc}$ = 15.6 Hz), 151.9 (d, $^{3}J_{pc}$ = 12.2 Hz), 156.1 (d, $^{1}J_{pc}$ = 36.9 Hz) ppm; $^{31}P\{^{1}H\}$ NMR (160 MHz, $C_6D_6$): $\delta$ = -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, $C_6D_6$, $Me_4Si$): $\delta$ = 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, $C_6D_6$,$Me_4Si$): $\delta$ = 26.1, 26.7, 30.9, 37.6, 48.5, 122.1, 123.2 (d, $^{4}J_{pc}$ = 1.6 Hz), 128.5, 128.9 (d, $^{3}J_{pc}$ = 6.8 Hz), 129.4, 134.4 (d, $^{2}J_{pc}$ = 20.1 Hz), 135.0 (d, $^{1}J_{pc}$ = 15.4 Hz), 151.9 (d, $^{3}J_{pc}$ = 11.9 Hz), 157.3 (d, $^{1}J_{pc}$ = 36.2 Hz) ppm; $^{31}P\{^{1}H\}$ NMR (160 MHz, $C_6D_6$): $\delta$ = -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$_6$H$_4$Me-4)$_2$}{NH-(CH$_2$)$_8$} (9q)**. Colorless solid, isolated yield 80% (177 mg); $^{1}$H NMR (400 MHz, $C_6D_6$, $Me_4Si$): $\delta$ = 1.30-1.92 (m, 14H; -(C$H_2$)$_7$-), 2.00 (s, 6H; Me), 4.45 (br, 1H; CH), 4.56 (d, $^{3}J$ = 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, $C_6D_6$,$Me_4Si$): $\delta$ = 21.1, 23.9, 25.7, 27.4, 32.1, 51.2, 122.1, 123.4 (d, $^{4}J_{pc}$ = 1.5 Hz), 128.5, 129.8 (d, $^{3}J_{pc}$ = 7.0 Hz), 132.1(d, $^{1}J_{pc}$ = 14.4Hz), 134.4 (d, $^{2}J_{pc}$ = 20.3 Hz), 139.4, 152.1 (d, $^{3}J_{pc}$ = 12.0 Hz), 156.5(d, $^{1}J_{pc}$ = 36.9Hz) ppm; $^{31}P\{^{1}H\}$ NMR (160 MHz, $C_6D_6$): $\delta$ = -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 93% (186 mg);.$^{1}$H NMR (400 MHz, $C_6D_6$, $Me_4Si$): $\delta$ = 1.28-1.85 (m, 14H; -(C$H_2$)$_7$-), 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, $C_6D_6$,$Me_4Si$): $\delta$ = 23.8, 25.7, 27.5, 31.9, 51.2, 122.2, 123.3 (d, $^{4}J_{pc}$ = 1.2 Hz), 128.5, 128.9 (d, $^{3}J_{pc}$ = 6.8 Hz), 129.4, 134.4 (d, $^{2}J_{pc}$ = 20.1 Hz), 135.3 (d, $^{1}J_{pc}$ = 15.6 Hz), 151.9 (d, $^{3}J_{pc}$ = 12.2 Hz), 156.1 (d, $^{1}J_{pc}$ = 37.5 Hz) ppm; $^{31}P\{^{1}H\}$ NMR (160 MHz, $C_6D_6$): $\delta$ = -14.3 ppm; HRMS: *m/z* calcd for $C_{27}H_{32}N_2P$: 415.2298 [M + H] $^{+}$; found: 415.2289.

**PhP{*i*PrN=C(NH*i*Pr)}$_2$ (9s)**. Colorless oil, isolated yield 93% (168 mg);.$^{1}$H NMR (400 MHz, $C_6D_6$, $Me_4Si$): $\delta$ = 0.98 (d, *J* = 6.1 Hz, 6H; CH(C$H_3$)$_2$), 1.08 (d, *J* = 6.1 Hz, 6H; CH(C$H_3$)$_2$), 1.22 (d, *J* = 6.1 Hz, 6H; CH(C$H_3$)$_2$), 1.34 (d, *J* = 6.1 Hz, 6H; CH(C$H_3$)$_2$), 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, $C_6D_6$,$Me_4Si$): $\delta$ = 22.4 (d, $^{4}J_{pc}$ = 2.9 Hz), 25.3 (d, $^{4}J_{pc}$ = 8.0 Hz), 42.9, 52.6 (d, $^{3}J_{pc}$ = 36.9 Hz), 129.2 (d, $^{3}J_{pc}$ = 6.4 Hz), 129.6, 133.3 (d, $^{1}J_{pc}$ = 17.6 Hz), 134.0 (d, $^{2}J_{pc}$ = 19.1 Hz), 151.4 (d, $^{1}J_{pc}$ = 35.4 Hz); $^{31}P\{^{1}H\}$ NMR (160 MHz, $C_6D_6$): $\delta$ = -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 on a SuperNova diffractometer using graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 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. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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## Notes and references

1 For selected reviews of CGAC reaction, see: (*a*) W.-X. Zhang, L. Xu and Z. Xi, *Chem. Commun*., 2015, **51**, 254; (*b*) C. Alonso-Moerno, A. Antiñolo, F. Carrillo-Hermosilla and A. Otero, *Chem. Soc. Rev*., 2014, **43**, 3406; (*c*) H. Shen and Z. Xie, *J. Organomet. Chem*., 2009, **694**, 1652; (*d*) W.-X. Zhang and Z. Hou, *Org. Biomol. Chem*., 2008, **6**, 1720.

2 For selected examples of CGAC reaction from our group, see: (*a*) P.-H. Wei, L. Xu, L.-C. Song, W.-X. Zhang and Z. Xi, *Organometallics,* **2014**, ***33****, 2784;* (*b*) F. Zhao, Y. Wang, W.-X. Zhang and Z. Xi, *Org. Biomol. Chem.,* **2012**, ***10***, 6266; (*c*) D. Li, Y. Wang, W.-X. Zhang, S. Zhang, J. Guang and Z. Xi, *Organometallics*, 2011, **30**, 5278; (d) D. Li, J. Guang, W.-X. Zhang and Z. Xi, *Org. Biomol. Chem*., 2010, **8**, 1816; (*e*) W.-X. Zhang, D. Li, Z. Wang and Z. Xi, *Organometallics*, 2009, **28**, 882.

3 For selected examples of CGAC reaction, see: (*a*) P. D. Schweizer, H. Wadepohl and L. H. Gade, *Oganometallics*, 2013, **32**, 3697; (*b*) J. Chen, Y. Wang and Y. Luo, *Chin. J. Chem*., 2013, **31**, 1065; (*c*) A. Grirrane, H. Garcia and E. Álvarez, *Beilstein. J. Org. Chem*., 2013, **9**, 1455; (*d*) A. Grirrane, H. Garcia, A. Corma and E. Álvarez, *Chem. - Eur. J*., 2012, **18**, 14934; (*e*) F. Han, Q. Teng, Y. Zhang, Y. Wang and Q. Shen, *Inorg. Chem*., 2011, **50**, 2634; (*f*) C. Alonso-Moreno, F. Carrillo-Hermosilla, A. Garcés, A. Otero, I. López-Solera, A. M. Rodríguez and A. Antiñolo, *Organometallics*, 2010, **29**, 2789; (*g*) J. Koller and R. G. Bergman, *Organometallics*, 2010, **29**, 5946; (*h*) J. R. Lachs, A. G. M. Barrett, M. R. Crimmin, G. Kociok-Köhn, M. S. Hill, M. F. Mahon and P. A. Procopiou, *Eur. J. Inorg. Chem*., 2008, 4173; (*i*) Z. Du, W. Li, X. Zhu, F. Xu and Q. Shen, *J. Org. Chem*., 2008, **73**, 8966; (*j*) Q. Li, S. Wang, S. Zhou, G. Yang, X. Zhu and Y. Liu, *J. Org. Chem*., 2007, **72**, 6763; (*k*) S. Zhou, S. Wang, G. Yang, Q. Li, L. Zhang, Z. Yao, Z. Zhou and H.-B. Song, *Oganometallics*, 2007, **26**, 3755; (*l*) W.-X. Zhang, M. Nishiura, Z. Hou, *Chem. Eur. J*., 2007, **13**, 4037; (*m*) H. Shen, H. -S. Chan and Z. Xie, *Organometallics*, 2006, **25**, 5515; (*n*) F. Montilla, D. del Río, A. Pastor and A. Galindo, *Organometallics,* 2006, **25**, 4996; (*o*) T.-G. Ong, J. S. O'Brien, I. Korobkov and D. S. Richeson, *Organometallics*, 2006, **25**, 4728; (*p*) W.-X. Zhang, M. Nishiura and Z. Hou, *Synlett*, 2006, 1213; (*q*) T.-G. Ong, G. P. A. Yap and D. S. Richeson, *J. Am. Chem. Soc*., 2003, **125**, 8100.

4 (*a*) V. Koshti, S. Gaikwad and S. H. Chikkali, *Coord. Chem. Rev.*, 2014, **265**, 52; (*b*) F. T. Edelmann, *Chem. Soc. Rev.*, 2012, **41**, 7657.

5 (*a*) R. J. Schwamm, B. M. Day, N. E. Mansfield, W. Knowelden, P. B. Hitchcock and M. P. Coles, *Dalton Trans*., 2014, **43**, 14302; (*b*) N. E. Mansfield, M. P. Coles and P. B. Hitchcock, *Polyhedron*, 2012, **37**, 9; (*c*) A. G. M. Barrett, M. R. Crimmin, M. S. Hill, P. B. Hitchcock, S. L. Lomas, M. F. Mahon and P. A. Procopiou, *Dalton Trans*., 2010, **39**, 7393; (*d*) G. Jin, C. Jones, P. C. Junk, K.-A. Lippert, R. P. Rose and A. Stasch, *New. J. Chem*., 2009, **33**, 64; (*e*) C. N. Rowley, T.-G. Ong, J. Priem, D. S. Richeson and T. K. Woo, *Inorg. Chem*., 2008, 47, 12024; (*f*) J. Grundy, N. E. Mansfield, M. P. Coles and P. B. Hitchcock, *Inorg. Chem*., 2008, **47**, 2258; (*g*) N. E. Mansfield, M. P. Coles and P. B. Hitchcock, *Dalton Trans*., 2006, 2052; (*h*) N. E. Mansfield, M. P. Coles, A. G. Avent and P. B. Hitchcock, *Organometallics*, 2006, **25**, 2470; (*i*) N. E. Mansfield, M. P. Coles and P. B. Hitchcock, *Dalton Trans*., 2005, 2833; (*j*) J. Grundy, M. P. Coles and P. B. Hitchcock, *Dalton Trans*., 2003, 2573. (*k*) M. P. Coles and P. B. Hitchcock, *Chem. Commun*., 2002, 2794.

6 (*a*) D. H. M. W. Thewissen and H. P. M. M. Ambrosius, *Recl. Trav. Chim. Pays-Bas*., 1980, **99**, 344; (*b*) H. P. M. M. Ambrosius, A. H. I. M. van der Linden and J. J. Steggerda, *J. Organomet. Chem*., 1981, **204**, 211; (*c*) K. Issleib, H. Schmidt and H. Meyer, *J. Organomet. Chem*., 1980, **192**, 33.

7 (*a*) R. S. P. Turbervill and J. M. Goicoechea, *Organometallics*, 2012, **31**, 2452; (*b*) R. S. P. Turbervill and J. M. Goicoechea, *Chem. Commun*., 2012, **48**, 1470.

8 C. A. Busacca, J. A. Milligan, E. Rattanangkool, C. Ramavarapu, A. Chen, A. K. Saha, Z. Li, H. Lee, S. J. Geib, G. Wang, C. H. Senanayake and P. Wipf, *J. Org. Chem*., 2014, **79**, 9878.

9 W. -X. Zhang, M. Nishiura and Z. Hou, *Chem. Commun*., 2006, 3812.

10 M. R. Crimmin, A. G. M. Barrett, M. S. Hill, P. B. Hitchcock and P. A. Procopiou, *Organometallics*, 2008, **27**, 497.

11 A. J. Roering, S. E. Leshinski, S. M. Chan, T. Shalumova, S. N. MacMillan, J. M. Tanski and R. Waterman, *Organometallics*, 2010, **29**, 2557;

12 W.-X. Zhang, M. Nishiura, T. Mashiko and Z. Hou, *Chem. - Eur. J.*, 2008, **14**, 2167.

13 A. C. Behrle and J. A. R. Schmidt, *Organometallics*, 2013, **32**, 1141.

14 (*a*) L. Xu, Z. Wang, W. -X. Zhang and Z. Xi, *Inorg. Chem*., 2012, **51**, 11941. See selected examples of rare-earth-metal anionic complexes: (*b*) I. Aillaud, C. Olier, Y. Chapurina, J. Collin, E. Schulz, R. Guillot, J. Hannedouche and A. Trifonov, *Organometallics*, 2011, **30**, 3378; (*c*) B. Xu, L. Huang, Z. Yang, Y. Yao, Y. Zhang and Q. Shen, *Organometallics*, 2011, **30**, 3588; (*d*) W. J. Evans, R. N. R. Broomhall-Dillard and J. W. Ziller, *Organometallics*, 1996, **15**, 1351.

15 N. E. Mansfield, J. Grundy, M. P. Coles, A. G. Avent and P. B. Hitchcock, *J. Am. Chem. Soc*., 2006, **128**, 13879.