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A Base-Stabilized Cationic Silyne with A π -Accepting Phosphonio Substituent

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ABSTRACT: A base-stabilized C-phosphonio-Si-amino-silyne **3** was synthesized, using an original method, through a coupling reaction between two Lewis-base-stabilized low-valent species: a silyliumylidene ion **1** and a P,S-bis-ylide **2** [C(o)-complex]. This new isolable cationic silyne **3** displays remarkably high stability at room temperature ($t_{1/2}$ = 7 days in THF) and a unique silyne reactivity thanks to the effect of phosphonio-substituent.

INTRODUCTION

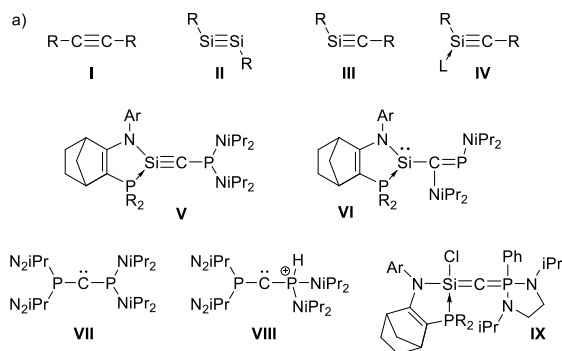


Figure 1. a) Alkyne (**I**) and heavier silicon analogues of alkynes (**II-V**) and related compounds (**VII-IX**).

Alkynes **I** with an easily functionalizable doubly unsaturated C≡C moiety is one of the most important organic functions, which are critical for building large and complicated molecular architectures.¹ Not surprisingly, heavier silicon analogues, disilynes **II** are also useful silicon based chemical tools (Figure 1a).² Since the first synthesis of stable disilynes independently by Sekiguchi's and Wiberg's groups in 2004,^{3,4} they have been intensively studied and several stable disilynes with different substituents such as silyl,^{3,5} aryl,⁶ alkyl⁷ or boryl⁸ groups are available. The particular reactivity of disilynes **II** closely related to their unique trans-bent structure featuring two non-degenerated π -bonds provides a new strategy to synthesize original molecules.² In contrast, the chemis-

try of silynes **III** is far underdeveloped since stable species remain elusive. Indeed, only a transient silyne has been reported as a possible intermediate by Apeloig et al.,⁹ and recently we have characterized at low temperature the base-stabilized silyne **V** which has demonstrated a significant carbenic character.¹⁰ However, **V** readily isomerizes above -30 °C via a 1,2-migration of a P-amino substituent to afford the corresponding phosphaketene derivative **VI**, strongly limiting the exploration of the reactivity. A similar isomerization, via a 1,2-migration of an amino group, was observed with (diphosphino)carbene **VII**,¹¹ and, in this case, the stability has been dramatically improved by substituting one of the phosphino-substituents by a π -accepting phosphonio group (**VIII**).¹² Thus, we have considered to use the same strategy to stabilize silynes, and here we report the synthesis of an isolable base-stabilized silyne **3**, using an original way, showing a remarkable stability at room temperature ($t_{1/2}$ = 7 days) and an enhanced reactivity. Of particular interest, the phosphonio-substituent contributes not only to the stabilization of silyne **3** but also to a unique chemical behavior.

RESULTS AND DISCUSSION

Synthesis and characterization of base-stabilized silyne 3. Previously we have demonstrated that the mixed P,S-bis-ylide **2**,¹³ because of the lability of sulfide ligand, undergoes substitution reactions at the central carbon atom with ambiphilic reagents¹⁴ such as a phosphine-stabilized silylene, which transforms the C(o)-complex into σ -silavinylidene phosphorane **IX**.¹⁵ Following the same synthetic strategy, the target silyne **3** has been prepared using a base-stabilized silyliumylidene ion **1** as ambiphilic reagent. Indeed, the reaction of P,S-bis-ylide **2** with chlorosilylene-supported silyliumylidene ion **1**¹⁶ in fluorobenzene (C₆H₅F) at room temperature readily affords the desired base-stabilized C-phosphonio-Si-amino-silyne **3** in 77 % yield (Scheme 1). The ³¹P-NMR spectrum displays an AB-system [3.1 ppm (P^{III}) and 25.6 ppm (P^{IV}), J_{PP} = 20.0 Hz]. In the ²⁹Si-NMR spectrum, a doublet of doublets signal with two large coupling constants appears at significantly low-field (-32.5 ppm, $^1J_{SiP}$ = 195.8 Hz, $^2J_{SiP}$ = 85.4 Hz) compared to the chemical shift of neutral C-phosphino-silyne **V** (-89.4 ppm), suggesting a decreased electron density at the

silicon center due to the π -accepting phosphonio-substituent at the carbon atom. In the ^{13}C -NMR spectrum, the signal for the central carbon atom appears as a doublet of doublets at 107.8 ppm ($J_{\text{CP}} = 156.4$ and 48.8 Hz) which is considerably low-field shifted relative to the P,S-bis-ylide **2** (16.6 ppm)¹³ or 1-silavinylidene phosphorane **IX** (27.5 ppm).¹⁵ This result is consistent with an increased SiC-multiple bond character, although this C-chemical shift appears at a higher field by 108.2 ppm than that of neutral silyne **V** (216 ppm).¹⁰

Scheme 1. The synthesis of (amino)(phosphonio)silyne **3**.

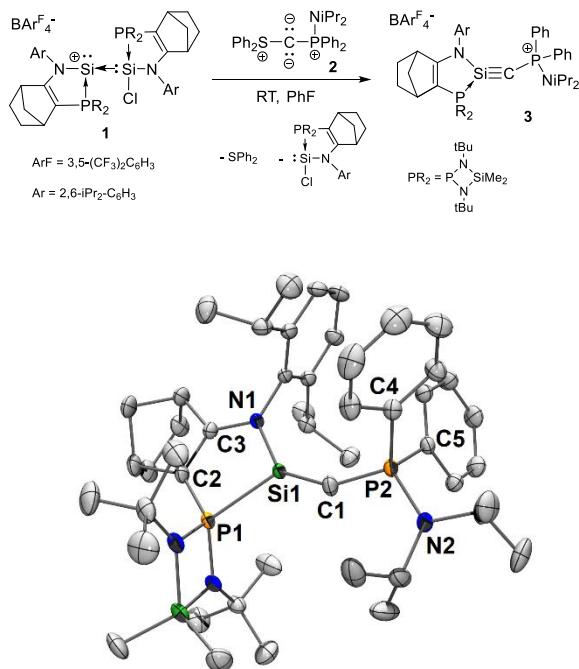


Figure 2. Molecular structure of **3**. Thermal ellipsoids represent 30 % probability. Disordered atoms, H atoms, solvent molecules and counter anion [BArF₄⁻, Ar^F = 3,5-(CF₃)₂C₆H₃] are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1-C1 1.631(2), C1-P2 1.666(2), N1-Si1 1.756(2), Si1-P1 2.258(1), P1-C2 1.722(2), C2-C3 1.380(3), C3-N1 1.375(3), P2-N2 1.663(2), P2-C4 1.812(2), P2-C5 1.821(3), Si1-C1-P2 148.3(2), N1-Si1-C1 139.7(1), C1-Si1-P1 126.7(1), N1-Si1-P1 93.5(1), Si1-P1-C2 92.7(1), P1-C2-C3 115.3(2), C2-C3-N1 125.4(2), C3-N1-Si1 113.1(2).

The X-ray structure of **3** confirms the intramolecular phosphine ligand bonded to the silicon center of silyne moiety resulting in a three-coordinate Si1 atom and a two-coordinate C1 atom (Figure 2).¹⁷ The silyne fragment exhibits a cis-configuration with bent geometries at both the Si1 atom [N1-Si1-C1: 139.7(1)°] and at the C1 atom [Si1-C1-P2: 148.3(2)°] contrary to the neutral silyne **V** showing a quasi-linear geometry around the silyne carbon atom (178.3°).¹⁰ The structure also exhibits a short Si1-C1 bond length [1.631(2) Å], which is shorter than SiC-double bonds (ca. 1.70 Å),^{18,19} and is in the range predicted for SiC-triple bonds (1.63 – 1.67 Å).^{20,21} This SiC-bond is even slightly shorter than that observed for the neutral silyne **V** (1.667 Å).¹⁰ The SiC bond in **3** is even shorter than that of the neutral silicon **V**, which is probably due to the strong polarization of the SiC π -bond (Si⁺=C⁻), increasing the electrostatic attraction between Si and C atoms. To our knowledge, this is the shortest SiC bond ever reported. The C1-P2 bond length [1.666(2) Å] is only slightly longer than

that observed for **IX** (1.623 Å) and carbodiphosphoranes (1.584 – 1.648 Å), suggesting a significant contribution of cumulene-type canonical structure (**3C**) in addition to the silyne character (**3A**) (Figure 3a). In contrast to the slightly pyramidalized silicon center in the neutral silyne **V** due to the π -electron donating phosphine-substituent, cationic silyne **3** exhibits a planar geometry around the three-coordinate Si1 atom ($\Sigma^\circ_{\text{Si1}} = 359.9^\circ$). The shortened Si1-N1 bond length [1.756(2) Å] relative to that observed for **V** (1.814 Å), due to the π -donation of amino group to the Si1 atom, suggests an increased electrophilic character at the silyne silicon center in **3**, compared to the neutral one **V**, certainly due to the π -accepting phosphonio substituent.

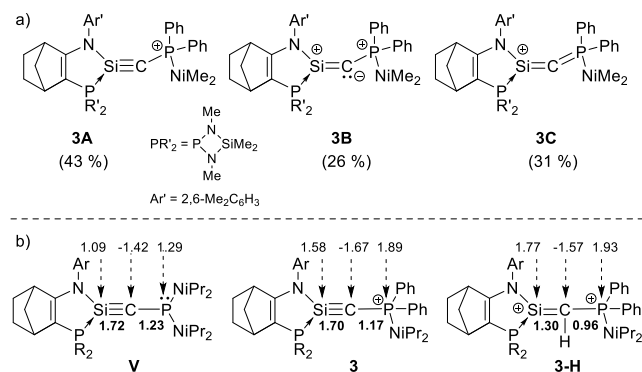


Figure 3. a) Canonical structures **3A,B,C** and the relative weights of the resonance forms estimated for the model compound **3'** (all methyl groups in **3** are replaced by H atoms) by NRT calculations. b) NPA charges and Wiberg bond indexes (in bold) of in the neutral and the cationic silynes **V** and **3** as well as in the protonated species **3-H**.

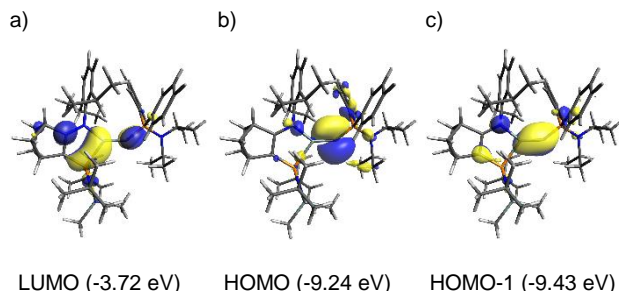


Figure 4. Frontier orbitals of **3** calculated at the Mo6-2X/Def2TZVP// Mo6-2X/6-31G(d) level of theory. a) LUMO. b) HOMO. c) HOMO-1

Theoretical study on the electronic structure of silyne 3. To gain more insight into the electronic structure of silyne **3**, DFT calculations have been performed at the Mo6-2X/6-31G(d) level of theory. The optimized structure of **3** agrees quite well with the experimental data, particularly the calculated bond lengths N1-Si1 (1.768 Å), Si1-P1 (2.257 Å), Si1-C1 (1.638 Å), C1-P2 (1.679 Å) as well as the Si1-C1-P2 bond angle (143.38°). The structure with a linear Si-C-P fragment is not minimum on the energy surface and is higher in energy by 8.8 kcal/mol. The HOMO-1 orbital corresponds to the SiC- π -bond orbital (Figure 4c) and the lowest unoccupied molecular orbital (LUMO) to the anti-bonding orbital (π^*_{SiC}) (Figure 4a). The highest occupied molecular orbital (HOMO) is mainly located at the central carbon atom as an in-plane lone

pair delocalizing to the adjacent Si and P atoms (Figure 4b), which is consistent with the experimental observation indicating that the electronic structure of **3** is intermediate between the two canonical forms silyne (**3A**) and cumulene (**3C**) (Figure 3). Certainly due to this effect, the HOMO-LUMO energy gap of **3** is considerably larger (5.52 eV) than that calculated for **V** (4.55 eV), in agreement with an enhanced thermal stability of **3**. The NBO analysis in the Si-C-P₂ moiety indicates the presence of a SiC-double bond and of a lone pair on the carbon atom [LP(C)] delocalizing toward the adjacent Si and P atoms, which is in agreement with the canonical structure **3B** (Figure 3). The two bonds between silicon and carbon atoms consist of a sp hybridized σ -bond [$sp^{1.22}(\text{Si})$ and $sp^{0.83}(\text{C})$] and a π -bond with pure p orbital. The second order perturbation analysis of **3** shows a larger donor-acceptor interaction energy for the LP(C)→Si interaction (61.2 kcal/mol) than the LP(C)→P₂ interaction (47.9 kcal/mol), which suggests a larger silyne character (**3A**) than Si=C=P cumulene (**3C**). This is probably due to the energetically lower σ^* -orbitals on the Si atom due to the weak P→Si bond as well as the more strongly polarized N-Si bond than N-P bond. A similar result is obtained in the analysis of the Intrinsic Bond Orbitals, in which the lone pair of C is more delocalized to Si than to P₂ (see the Supporting Information). Indeed, the considerably elevated multiple-bonding character of SiC-moiety in **3** was demonstrated by the large Wiberg bond index (WBI) of the SiC-bond (1.70) (Figure 3b). This value is close to the WBI calculated for the neutral base-stabilized silyne **V** (WBI_{SiC}: 1.72). Furthermore, a protonation on the C atom to form **3H** (Figure 3a) results in a more significant increase of the positive charge on the Si atom than that on the P atom [$\Delta\text{NPA}_{3\rightarrow 3\text{H}}$: 0.2 (Si) and 0.04 (P)]. Similarly, upon protonation, the WBI of the SiC bond was more strongly reduced than that of the CP bond [$\Delta\text{WBI}_{3\rightarrow 3\text{H}}$: -0.40 (SiC bond) and -0.21 (CP bond)]. These results are in good agreement with the fact that the LP(C)→Si π -interaction is a major interaction and more important than the LP(C)→P interaction. Indeed, the NRT analysis performed on **3'** (model compound in which all methyl groups are replaced by hydrogen atoms) also indicates a more important contribution of silyne structure **3A** (43 %) than the cumulene resonance **3C** (31 %) (Figure 3a). As expected, due to the presence of an accepting phosphonio-substituent, a large positive charge (+1.58) resides on the Si atom in **3**, which is much larger than that calculated for **V** (+1.09). Therefore, silyne **3** should present a strong electrophilic character at the Si atom.

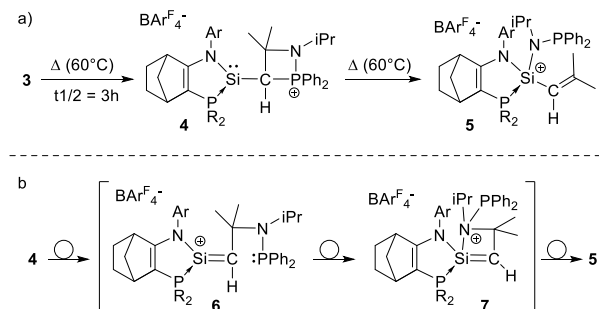


Figure 5. a) Thermal isomerization of **3**. b) Proposed mechanisms for the isomerization of **4** to **5**.

Reactivity of silyne 3. Although silyne **3** is quite persistent at room temperature, it slowly isomerizes *via* a formal C-H

bond activation at the carbon atom of silyne to give an amino(alkyl)silylene **4** with a four-membered cyclic phosphonium substituent (Figure 5a). Silylene **4** evolves further leading to a phosphine-stabilized bis-amino(vinyl)silylium ion **5**. The half-life time of **3** at 25 °C in THF is about 7 days, and as indicated by the ³¹P-NMR spectroscopy the formation of compounds **4** and **5** was observed almost at the same rate at the early stage of transformation. At 60 °C, the isomerization completes in 8 hours. The second step of the isomerization is probably triggered by the π -donation of silylene inducing the decomplexation of phosphine leading to a transient silenenylium cation **6** (Figure 5b). Intermediate **6** is then stabilized by the intramolecular nucleophilic attack of the resulting amine to the electrophilic Si atom to form **7**, which evolves further by ring-opening *via* cyclobutene-butadiene type isomerization to afford the final product **5**.

Scheme 2. The reactions of silyne 3.

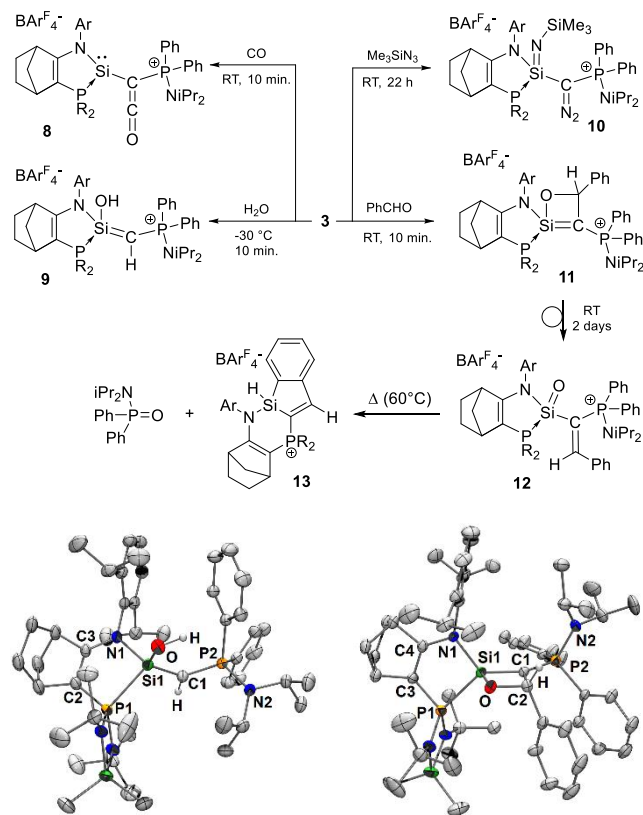


Figure 6. Molecular structure of **9** (left) and **11** (right). Thermal ellipsoids represent 30 % probability. Disordered, H atoms, solvent molecules and counter anion [$\text{BAr}^{\text{F}_4^-}$, $\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$] are omitted for clarity. Selected bond lengths [Å] and angles [°]: **9**: Si1-O 1.647(2), Si1-C1 1.765(3), C1-P2 1.682(3), N1-Si1 1.790(2), Si1-P1 2.346(1), Si1-C1-P2 129.4(2). **11**: Si1-C1 1.765(4), C1-C2 1.545(5), C2-O 1.483(4), O-Si1 1.653(2), C1-P2 1.692(4), Si1-P1 2.358(1), N1-Si1 1.772(3), Si1-C1-C2 86.1(2), Si1-C1-P2 150.4(2), P2-C1-C2 123.0(3), C1-C2-O 97.8(3), C2-O1-Si1 92.3(2), O-Si1-C1 83.7(2).

Certainly because of the relatively large $\Delta E_{\text{HOMO-LUMO}}$, silyne **3** does not react with non-polar and poorly reactive reagents such as H_2 , N_2 and ethylene, even at 60 °C. In contrast, **3** shows a high reactivity towards various polarized reagents.

Indeed, it readily reacts, at room temperature, with CO on the silyne carbon atom to give ketene **8** featuring a silylene and a phosphonio substituents. The presence of ketene function is indicated by a typical ^{13}C -NMR pattern with a strongly shielded β -carbon signal (8.2 ppm, $J_{\text{CP}} = 124.8$ Hz) and a deshielded α -carbon signal (168.8 ppm, $J_{\text{CP}} = 8.2$ and 14.4 Hz).²² This result shows a carbene-like reactivity of **3**.²³ As expected due to the important electropositive charge at the Si center,^{18a,24} silyne **3** exhibits an electrophilic character, and therefore it smoothly reacts with H_2O via a 1,2-addition on the silyne moiety to give the base-supported 1-silaenol **9**. The formation of enol form rather than silanone tautomer, was confirmed by X-ray diffraction analysis, showing a SiO-single bond [Si1-O: 1.647(2) Å] and a short SiC-double bond [Si1-C1: 1.765(3) Å] (Figure 6-left). The reaction of silyne **3** with a trimethylsilylazide (Me_3SiN_3) results in the formation of (silaime)(phosphonio) diazometane **10**. The IR spectroscopy shows a strong and characteristic absorption band of diazo function at 2073 cm^{-1} . The reaction certainly proceeds via a [3+2]-cycloaddition followed by the ring-opening of silatriazole intermediate **14** to afford the corresponding diazomethane derivative **10** (Figure 7a).

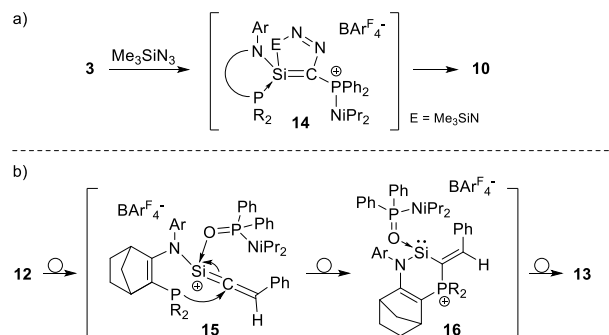


Figure 7. Proposed mechanisms for a) the reactions of **3** with Me_3SiN_3 , b) the isomerization of **12** to **13**.

Silyne **3** undergoes a [2+2]-cycloaddition with benzaldehyde to give the corresponding 4-membered cycloadduct **11** (Scheme 2), which is persistent enough at room temperature to be isolated and characterized by X-ray diffraction analysis (Figure 6-right). However, **11** slowly isomerizes at room temperature to form alkene **12** substituted by a silanone and a phosphonio fragments via a cyclobutene-butadiene process. The reaction completes in 2 days at room temperature. At 60 °C, **12** isomerizes further to cleanly afford a polycyclic silane **13** releasing phosphine oxide as by-product. The isomerization of **12** probably starts with an intramolecular attack of silanone on the phosphonio fragment to substitute the alkene moiety to generate 1-silaallene **15** (a formal deoxygenation reaction by the phosphonio fragment) (Figure 7b). Intermediate **15** then isomerizes further via phosphine migration from silicon to the central allene carbon atom to generate a phosphine oxide-stabilized cyclic silylene **16**, followed by its insertion into a C-H bond of phenyl group to afford **13** and phosphine oxide. **13** has been isolated and fully characterized in solution and in the solid state (supporting information).

CONCLUSION

In conclusion, we successfully synthesized a base-stabilized C-phosphonio-Si-amino-silyne **3** through a coupling reaction between two Lewis-base-stabilized low-valent species: a si-

lyliumylidene ion **1** and a P,S-bis-ylide **2**. Compared to the previously reported neutral silyne **V**, this new cationic silyne **3** exhibits an enhanced stability at room temperature ($t_{1/2} = 7$ days), and a high and rich reactivity enabling the synthesis of new molecules with original functions. The phosphonio substituent proved useful in increasing not only the stability but also the reactivity pattern of **3** due to its dual reactivity. Further studies on the application of this new silyne **3** are under active investigation.

EXPERIMENTAL SECTION

General procedures. All manipulations were performed under inert atmosphere of argon by using Schlenk or high-pressure NMR tube techniques. Dry, oxygen-free solvents were employed. ^1H , ^{11}B , ^{19}F , ^{13}C , ^{29}Si and ^{31}P NMR spectra were recorded on Bruker Avance II 300MHz, Avance III HD 400 MHz and Avance I and II 500 MHz spectrometers. ^1H , ^{29}Si and ^{13}C NMR chemical shifts are reported in ppm relative to SiMe_4 as internal standard. ^{31}P NMR chemical shifts are expressed in ppm relative to 85 % H_3PO_4 . ^{11}B chemical shifts are relative to $\text{BF}_3\cdot\text{OEt}_2$ and ^{19}F chemical shifts are relative to CFCl_3 as external reference. The following abbreviations and their combinations are used: br, broad; s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet. ^1H and ^{13}C resonance signals were attributed by means of 2D COSY, HSQC and HMQC experiments. The phosphine-stabilized silyliumylidene **16** was synthesized as previously reported.

Synthesis of chloro(diisopropylamino)diphenylphosphonium chloride (A): To a Et_2O solution (40 mL) of C_2Cl_6 (11.8 g, 50 mmol) was added at -80 °C a Et_2O solution (40 mL) of diisopropylaminodiphenylphosphine (14 g, 50 mmol). After stirring for 5 min, the solution was slowly warmed to RT (an abundant white precipitate appeared). After 1 hours, precipitated white solid was washed with Et_2O (2 x 40 mL). The residue were dried under reduced pressure to obtain **A** as white powder (13.2 g, 74 %). ^1H NMR (300 MHz, 25 °C, CDCl_3): $\delta = 1.37$ (d, $J_{\text{HH}} = 6.8$ Hz, 12H, $\text{CH}_{3\text{IPr}}$), 3.87 (dsept, $J_{\text{HH}} = 6.8$ Hz, $J_{\text{HP}} = 20.8$ Hz, 2H, CH_{IPr}), 7.80–7.85 (m, 6H, CH_{Ar}), 8.36–8.44 (m, 4H, CH_{Ar}). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, 25 °C, CDCl_3): $\delta = 22.7$ (d, $J_{\text{CP}} = 4.5$ Hz, $\text{CH}_{3\text{IPr}}$), 52.7 (d, $J_{\text{CP}} = 0.9$ Hz, CH_{IPr}), 122.1 (d, $J_{\text{CP}} = 122.8$ Hz, P- C_{Ar}), 130.9 (d, $J_{\text{CP}} = 15.6$ Hz, $\text{CH}_{\text{Ar-PPH}}$), 133.5 (d, $J_{\text{CP}} = 13.2$ Hz, $\text{CH}_{\text{Ar-PPH}}$), 136.7 (d, $J_{\text{CP}} = 3.5$ Hz, $\text{CH}_{\text{Ar-PPH}}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, 25 °C, CDCl_3): $\delta = 67.8$ (P^+).

Synthesis of protonated P,S-ylide (B). To a THF (80 mL) suspension of methyldiphenylsulfonium triflate (8.6 g, 24.6 mmol) was added dropwise at -80 °C n-BuLi (15.5 mL, 1.6 M solution in hexanes, 24.6 mmol). After stirring for 30 min, this solution was added to a cold THF solution (60 mL, -80 °C) of phosphonium salt **A** (3.8 g, 16.5 mmol). The mixture was then slowly warmed to RT. After removal of all the volatiles under vacuum, the resulting white solid were extracted with CH_2Cl_2 (ca. 50 mL) and were concentrated under reduced pressure. Addition of Et_2O (ca. 60 mL) resulted in the precipitation of **B**. The precipitate were washed with Et_2O (ca. 20 mL) and dried to obtain **B** as a white solid (4.7 g, 69 %). ^1H NMR (300 MHz, 25 °C, CDCl_3): $\delta = 1.08$ (d, $J_{\text{HH}} = 6.8$ Hz, 12H, $\text{CH}_{3\text{IPr}}$), 3.30 (d, $J_{\text{HP}} = 15.0$ Hz, 1H, S-CH-P), 3.50 (dsept, $J_{\text{HH}} = 6.8$ Hz, $J_{\text{HP}} = 17.3$ Hz, 2H, CH_{IPr}), 7.40–7.46 (m, 10H, CH_{Ar}), 7.55–7.76 (m, 10H, CH_{Ar}). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, 25 °C, CDCl_3): $\delta = 15.7$ (d, $J_{\text{CP}} = 147.4$ Hz, S-CH-P), 23.2 (d, $J_{\text{CP}} = 2.1$ Hz, $\text{CH}_{3\text{IPr}}$), 48.5 (d, $J_{\text{CP}} = 5.2$ Hz, CH_{IPr}), 127.0 (d, $J_{\text{CP}} = 110.5$ Hz, P- C_{Ar}), 127.4 ($\text{CH}_{\text{Ph-SPh}}$), 129.5 (d, $J_{\text{CP}} = 12.8$ Hz, $\text{CH}_{\text{Ph-PPH}}$),

130.4 (CH_{ph-SPh}), 131.8 (CH_{ph-SPh}), 132.3 (d, J_{CP} = 10.1 Hz, CH_{ph-PPH}), 133.3 (d, J_{CP} = 3.1 Hz, CH_{ph-PPH}), 136.7 (d, J_{CP} = 5.2 Hz, S-C_{Ar}). ³¹P{¹H} NMR (121 MHz, 25 °C, CDCl₃): δ = 39.8 (P⁺).

Synthesis of 2: To a mixture of **B** (400 g, 0.616 mmol) and KHMDS (110 mg, 0.552 mmol) was added THF (5 mL) at -50 °C. The solution was kept stirring for 30 min at this temperature. After removal of all the volatiles under vacuum, the phosphonium-sulfonium bis-ylide **2** was extracted with pentane (ca. 25 mL) and the volatiles were removed under reduced pressure. The residue were dissolved in pentane (0.5 mL) and stored at -30 °C to precipitate **2** as yellow powder (230 mg, 86 %). ¹H NMR (300 MHz, 25 °C, C₆D₆): δ = 1.17 (d, J_{HH} = 6.8 Hz, 12H, CH_{3iPr}), 3.62 (dsept, J_{HH} = 6.8 Hz, J_{HP} = 15.6 Hz, 2H, CH_{iPr}), 6.85-6.90 (m, 2H, CH_{Ar}), 6.87-7.03 (m, 4H, CH_{Ar}), 7.12-7.22 (m, 6H, CH_{Ar}), 7.87-7.90 (m, 4H, CH_{Ar}), 8.01-8.08 (m, 4H, CH_{Ar}). ¹³C{¹H} NMR (75 MHz, 25 °C, C₆D₆): δ = 23.6 (d, J_{CP} = 2.1 Hz, CH_{3iPr}), 34.2 (br s, S-C-P), 47.4 (d, J_{CP} = 4.2 Hz, CH_{iPr}), 126.6 (CH_{ph-SPh}), 127.9 (d, J_{CP} = 11.1 Hz, CH_{ph-PPH}), 128.5 (CH_{ph-SPh}), 128.6 (CH_{ph-SPh}), 129.4 (d, J_{CP} = 2.8 Hz, CH_{ph-PPH}), 132.1 (d, J_{CP} = 9.0 Hz, CH_{ph-PPH}), 136.8 (d, J_{CP} = 96.1 Hz, P-C_{Ar}), 150.3 (d, J_{CP} = 22.2 Hz, S-C_{Ar}). ³¹P{¹H} NMR (121 MHz, 25 °C, C₆D₆): δ = 32.0 (P⁺).

Synthesis of 3: In a Schlenk tube, to a mixture of **1** (700 mg, 0.359 mmol, 0.9 eq) and bis(ylide) **2** (192 mg, 0.397 mmol), 5 mL of fluorobenzene was added at ambient temperature. After 10 min, all the volatiles were removed under reduced pressure. Then, **3** was obtained as red crystals in THF/Et₂O (1 mL + 5 mL) at -30 °C (605 mg, 77%). Mp. 124-126 °C (decomp.). Crystals suitable for X-ray diffraction were obtained from saturated THF/Et₂O solution at -30 °C. ¹H NMR (300 MHz, 25 °C, THF-*d*₈): δ = 0.57 (s, 3H, SiMe₂), 0.72 (s, 3H, SiMe₂), 0.91 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 0.95 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.12 (d, J_{HH} = 6.8 Hz, 6H, CH_{3iPr-NiPr}), 1.14 (d, J_{HH} = 6.8 Hz, 6H, CH_{3iPr-NiPr}), 1.17 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.18 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.39 (s, 18H, CH_{3tBu}), 1.39 (overlapped, 1H, CH_{2Norb}), 1.54 (m, 1H, CH_{2Norb}), 1.69 (m, 2H, CH_{2Norb}), 1.90 (m, 2H, CH_{2Norb}), 2.74 (m, 1H, CH_{bridgehead}), 3.00 (sept, J_{HH} = 6.8 Hz, 1H, CH_{iPr-Dip}), 3.02 (sept, J_{HH} = 6.8 Hz, 1H, CH_{iPr-Dip}), 3.38 (m, 1H, CH_{bridgehead}), 3.46 (dsept, J_{HP} = 16.9 Hz, J_{HH} = 6.8 Hz, 2H, CH_{iPr-NiPr}), 7.20-7.26 (m, 2H, CH_{Ar}), 7.29-7.40 (m, 5H, CH_{Ar}), 7.42-7.46 (m, 3H, CH_{Ar}), 7.56-7.67 (m, 3H, CH_{Ar}), 7.60 (s, 4H, *p*-CH_{BAr}), 7.82 (s, 8H, *m*-CH_{BAr}). ¹³C{¹H} NMR (125 MHz, 25 °C, THF-*d*₈): δ = 3.9 (d, J_{CP} = 1.6 Hz, SiMe₂), 4.4 (SiMe₂), 23.2 (d, J_{CP} = 2.3 Hz, CH_{iPr-NiPr}), 23.3 (d, J_{CP} = 2.3 Hz, CH_{3iPr-NiPr}), 23.4 (CH_{3iPr-Dip}), 23.5 (CH_{3iPr-Dip}), 24.5 (CH_{3iPr-Dip}), 24.9 (CH_{3iPr-Dip}), 25.2 (CH_{2Norb}), 28.2 (CH_{2Norb}), 29.4 (CH_{iPr-Dip}), 29.8 (CH_{iPr-Dip}), 32.2 (d, J_{CP} = 6.4 Hz, CH_{3tBu}), 32.3 (d, J_{CP} = 6.4 Hz, CH_{3tBu}), 42.0 (CH_{iPr-NiPr}), 45.7 (d, J_{CP} = 8.1 Hz, CH_{bridgehead}), 48.2 (d, J_{CP} = 6.9 Hz, CH_{2Norb}), 48.5 (d, J_{CP} = 5.2 Hz, CH_{bridgehead}), 53.4 (C_{tBu}), 53.4 (C_{tBu}), 97.3 (dd, J_{CP} = 73.1 and 2.6 Hz, NC=C_P), 107.8 (dd, J_{CP} = 156.4 and 48.8 Hz, Si≡C-P), 118.0 (br sept, J_{CF} = 4.3 Hz, *p*-CH_{BAr}), 125.1 (CH_{Ar-Dip}), 125.2 (CH_{Ar-Dip}), 125.3 (q, J_{CF} = 272.2 Hz, CF₃), 129.1 (d, J_{CP} = 12.7 Hz, CH_{Ar-PPH}), 129.1 (d, J_{CP} = 12.7 Hz, CH_{Ar-PPH}), 129.8 (CH_{Ar-Dip}), 129.9 (qq, J_{CF} = 31.2 Hz, J_{CB} = 2.9 Hz, *m*-CH_{BAr}), 131.7 (d, J_{CP} = 2.3 Hz, CH_{Ar-PPH}), 131.7 (d, J_{CP} = 2.3 Hz, CH_{Ar-PPH}), 132.2 (d, J_{CP} = 11.0 Hz, CH_{Ar-PPH}), 132.3 (d, J_{CP} = 11.0 Hz, CH_{Ar-PPH}), 134.1 (d, J_{CP} = 3.5 Hz, N-C_{Ar}), 134.2 (d, J_{CP} = 108.5 Hz, P-C_{Ar}), 134.6 (d, J_{CP} = 109.3 Hz, P-C_{Ar}), 135.4 (o-CH_{BAr}), 146.7 (iPr-C_{Ar}), 146.8 (iPr-C_{Ar}), 162.7 (q, J_{CB} = 50.0 Hz, *isop*-C_{BAr}), 189.0 (d, J_{CP} = 19.1 Hz, NC=C_P). ³¹P{¹H} NMR (121 MHz, 25 °C, THF-*d*₈): δ = 1.1 (d, J_{PP} = 20.0 Hz, Si-satellite:

J_{PSi} = 194.9 Hz, Si-P), 25.6 (d, J_{PP} = 20.0 Hz, Si-satellite: J_{PSi} = 85.6 Hz, ⁺PPH₂). ²⁹Si{¹H} NMR (99 MHz, 25 °C, THF-*d*₈): δ = 13.5 (d, J_{CP} = 3.1 Hz, SiMe₂), -32.5 (dd, J_{SiP} = 195.0 and 85.4 Hz, N-Si-P). ¹B{¹H} (160 MHz, 25 °C, THF-*d*₈): δ = -6.5 (BAr). ¹⁹F (470 MHz, 25 °C, THF-*d*₈): δ = -63.3 (CF₃).

Isomerization of 3. In an NMR tube, THF (0.4 mL) solution of **3** (80 mg, 0.0474 mmol) was kept at 25 °C or heated at 60 °C. This reaction was monitored by ³¹P NMR. The isomerization of **3** into **5** completed after 18 days at 25 °C or 8 hours at 60 °C. Once the proportion of **4** to the others (**3** and **5**) was maximized (2 hours at 60 °C), **4** was characterized by NMR as a mixture with **4**, and **5**. After 8 hours at 60 °C, **5** was obtained as colorless crystals (62 mg, 78%) in THF/pentane (0.3 mL + 1 mL) at -30 °C. Mp. 190-192 °C (decomp.). Crystals suitable for X-ray diffraction were obtained from saturated Et₂O/pentane solution at -30 °C.

Data for **4**: ¹H NMR (500 MHz, 25 °C, THF-*d*₈): δ = 1.54 (overlapped, 1H, Si-CH-P). ¹³C{¹H} NMR (125 MHz, 25 °C, THF-*d*₈): δ = 3.8 (d, J_{CP} = 2.9 SiMe₂), 6.0 (d, J_{CP} = 4.1 Hz, SiMe₂), 22.7 (CH_{3iPr-NiPr}), 29.7 (d, J_{CP} = 6.9 Hz, SiCH-CMe₂), 23.8 (CH_{3iPr-NiPr}), 31.7 (SiCH-CMe₂), 31.8 (dd, J_{CP} = 23.7 and 6.5 Hz, Si-CH-P), 32.8 (d, J_{CP} = 5.2 Hz, CH_{3tBu}), 33.6 (d, J_{CP} = 3.5 Hz, CH_{3tBu}), 43.1 (d, J_{CP} = 5.2 Hz, CH_{bridgehead}), 46.9 (d, J_{CP} = 3.5 Hz, CH_{bridgehead}), 48.6 (d, J_{CP} = 4.1 Hz, CH_{2Norb}), 52.0 (C_{tBu}), 53.4 (d, J_{CP} = 2.3 Hz, C_{tBu}), 73.5 (dd, J_{CP} = 12.1 and 6.4 Hz, SiCH-CMe₂), 103.3 (dd, J_{CP} = 36.4 and 3.6 Hz, NC=C_P), 177.0 (d, J_{CP} = 32.9 Hz, NC=C_P). ³¹P{¹H} NMR (202 MHz, 25 °C, THF-*d*₈): δ = 59.6 (d, J_{PP} = 106.4 Hz, P⁺), 77.3 (d, J_{PP} = 106.4 Hz, Si-satellite: J_{PSi} = 209.8 Hz, P→Si). ²⁹Si{¹H} NMR (99 MHz, 25 °C, THF-*d*₈): δ = 10.0 (d, J_{CP} = 3.0 Hz, SiMe₂), -17.8 (dd, J_{SiP} = 208.9 and 40.0 Hz, N-Si-P).

Data for **5**: Major(97%) : ¹H NMR (500 MHz, 25 °C, THF-*d*₈): δ = 0.52 (d, J_{HH} = 6.7 Hz, 3H, CH_{3iPr-NiPr}), 0.72 (s, 3H, SiMe₂), 0.73 (s, 3H, SiMe₂), 1.05 (d, J_{HH} = 6.3 Hz, 3H, CH_{3iPr-NiPr}), 1.10 (d, J_{HP} = 1.2 Hz, 9H, CH_{3tBu}), 1.14 (d, J_{HH} = 6.6 Hz, 3H, CH_{3iPr-Dip}), 1.16 (d, J_{HH} = 6.6 Hz, 3H, CH_{3iPr-Dip}), 1.23 (d, J_{HH} = 6.6 Hz, 3H, CH_{3iPr-Dip}), 1.44 (d, J_{HP} = 2.3 Hz, 3H, C=CMe), 1.55 (s, 9H, CH_{3tBu}), 1.61 (d, J_{HH} = 9.1 Hz, 1H, CH_{2Norb}), 1.65 (m, 1H, CH_{2Norb}), 1.69 (d, J_{HH} = 6.7 Hz, 3H, CH_{3iPr-Dip}), 1.77 (m, 1H, CH_{2Norb}), 1.91 (d, J_{HH} = 9.1 Hz, 1H, CH_{2Norb}), 1.96 (dd, J_{HP} = 2.5 Hz, J_{HH} = 1.1 Hz, 3H, C=CMe), 1.96 (overlapped, 1H, CH_{2Norb}), 2.00 (overlapped, 1H, CH_{2Norb}), 2.85 (m, 1H, CH_{bridgehead}), 3.07 (sept, J_{HH} = 6.7 Hz, 1H, CH_{iPr-Dip}), 3.39 (br sept, J_{HH} = 6.6 Hz, 1H, CH_{iPr-NiPr}), 3.45 (m, 1H, CH_{bridgehead}), 3.73 (sept, J_{HH} = 6.7 Hz, 1H, CH_{iPr-Dip}), 5.63 (s, 1H, Si-CH=C), 7.32-7.40 (m, 4H, CH_{Ar}), 7.40-7.45 (m, 7H, CH_{Ar}), 7.72-7.75 (m, 2H, CH_{Ar}), 7.82 (s, 4H, *p*-CH_{BAr}), 7.96 (s, 8H, *m*-CH_{BAr}). ¹³C{¹H} NMR (125 MHz, 25 °C, THF-*d*₈): δ = 3.4 (dd, J_{CP} = 2.3 and 8.7 Hz, SiMe₂), 6.9 (SiMe₂), 23.1 (CH_{iPr-Dip}), 23.8 (CH_{3iPr-NiPr}), 24.7 (CH_{3iPr-Dip}), 25.1 (C=C-CH₃), 26.4 (CH_{3iPr-Dip}), 26.8 (CH_{3iPr-NiPr}), 27.3 (d, J_{CP} = 2.0 Hz, CH_{2Norb}), 27.4 (CH_{3iPr-Dip}), 27.9 (CH_{2Norb}), 29.0 (CH_{iPr-Dip}), 29.5 (CH_{iPr-Dip}), 30.8 (C=C-CH₃), 32.6 (d, J_{CP} = 6.4 Hz, CH_{3tBu}), 33.2 (d, J_{CP} = 5.2 Hz, CH_{3tBu}), 42.7 (d, J_{CP} = 4.1 Hz, CH_{bridgehead}), 46.7 (d, J_{CP} = 8.7 Hz, CH_{bridgehead}), 48.3 (d, J_{CP} = 2.9 Hz, CH_{2Norb}), 52.9 (C_{tBu}), 54.0 (CH_{iPr-NiPr}), 54.1 (d, J_{CP} = 2.3 Hz, C_{tBu}), 100.9 (dd, J_{CP} = 58.4 and 5.8 Hz, NC=C_P), 118.0 (br sept, J_{CF} = 4.1 Hz, *p*-CH_{BAr}), 125.1 (CH_{Ar-Dip}), 122.5 (dd, J_{CP} = 36.7 and 2.6 Hz, Si-CH=C), 125.4 (q, J_{CF} = 272.3 Hz, CF₃), 127.0 (CH_{Ar-Dip}), 128.4 (d, J_{CP} = 5.2 Hz, CH_{Ar-PPH}), 129.3 (CH_{Ar-PPH}), 129.3 (d, J_{CP} = 6.4 Hz, CH_{Ar-PPH}), 129.9 (qq, J_{CF} = 31.8 Hz, J_{CB} = 2.9 Hz, *m*-CH_{BAr}), 130.1 (CH_{Ar-Dip}), 131.8 (d, J_{CP} = 16.8 Hz, CH_{Ar-PPH}), 132.4 (CH_{Ar-PPH}), 135.2 (d, J_{CP} = 16.2 Hz, P-C_{Ar}), 135.4 (o-

CH_{BAr}), 136.8 (d, J_{CP} = 2.9 Hz, N-C_{Ar}), 137.8 (d, J_{CP} = 25.4 Hz, CH_{Ar-PPh}), 139.8 (dd, J_{CP} = 16.2 and 2.3 Hz, P-C_{Ar}), 147.7 (iPr-C_{Ar}), 148.7 (iPr-C_{Ar}), 162.7 (q, J_{CB} = 49.7 Hz, *isop*-C_{BAr}), 163.6 (d, J_{CP} = 7.5 Hz, C=C_{Me₂}), 188.8 (d, J_{CP} = 24.3 Hz, NC=C_P). ³¹P{¹H} NMR (202 MHz, 25 °C, THF-*d*₈): δ = 39.1 (d, J_{PP} = 94.5 Hz, Si-satellite: J_{PSi} = 209.7 Hz, P-Si), 54.6 (d, J_{PP} = 94.5 Hz, N-P⁺PPH₂). ²⁹Si{¹H} NMR (99 MHz, 25 °C, THF-*d*₈): δ = 19.2 (dd, J_{CP} = 3.0 and 1.4 Hz, SiMe₂), -30.7 (dd, J_{SiP} = 209.2 and 40.7 Hz, N-Si-P). ¹B{¹H} (160 MHz, 25 °C, THF-*d*₈): δ = -6.5 (BAr). ¹⁹F (470 MHz, 25 °C, THF-*d*₈): δ = -63.3 (CF₃). Minor: (3%): ¹³C{¹H} NMR (125 MHz, 25 °C, THF-*d*₈): δ = 3.7 (d, J_{CP} = 5.7 Hz, SiMe₂), 7.3 (SiMe₂), 25.8 (CH_{2Norb}), 27.9 (CH_{2Norb}), 28.7 (CH_{iPr-Dip}), 31.4 (C=C-CH₃), 32.8 (d, J_{CP} = 4.6 Hz, CH_{3tBu}), 43.0 (d, J_{CP} = 4.7 Hz, CH_{bridgehead}), 50.1 (d, J_{CP} = 8.1 Hz, CH_{2Norb}), 53.0 (C_{tBu}), 54.2 (CH_{iPr-NiPr}), 54.4 (d, J_{CP} = 1.6 Hz, C_{tBu}), 103.4 (dd, J_{CP} = 57.3 and 6.4 Hz, NC=C_P), 122.4 (dd, J_{CP} = 34.5 and 3.0 Hz, Si-CH=C), 125.6 (CH_{Ar-Dip}), 126.9 (CH_{Ar-Dip}), 128.7 (d, J_{CP} = 5.0 Hz, CH_{Ar-PPh}), 130.9 (CH_{Ar-Dip}), 132.5 (CH_{Ar-PPh}), 134.7 (d, J_{CP} = 16.3 Hz, P-C_{Ar}), 137.2 (d, J_{CP} = 4.1 Hz, N-C_{Ar}), 137.6 (d, J_{CP} = 26.2 Hz, CH_{Ar-PPh}), 147.7 (iPr-C_{Ar}), 148.1 (iPr-C_{Ar}), 189.2 (d, J_{CP} = 24.9 Hz, NC=C_P). ³¹P{¹H} NMR (202 MHz, 25 °C, THF-*d*₈): δ = 41.3 (d, J_{PP} = 100.8 Hz, P-Si), 54.9 (d, J_{PP} = 102.0 Hz, N-P⁺PPH₂). ²⁹Si{¹H} NMR (99 MHz, 25 °C, THF-*d*₈): δ = 19.7 (br s, SiMe₂), -27.0 (dd, J_{SiP} = 214.2 and 38.9 Hz, N-Si-P).

Synthesis of 8: ATHF (0.4 ml) solution of **3** (90 mg, 0.054 mmol) was exposed to a 5 bar of CO at room temperature. After 5 minutes, all volatiles were removed under vacuum to obtain **8** as yellow powder (90 mg, 99%). Crystals suitable for X-ray diffraction analysis were grown from saturated C₆H₅F/pentane solution at -30 °C. Mp. 155-157 °C (decomp.). Major (53%): ¹H NMR (400 MHz, -30 °C, THF-*d*₈): δ = 0.66 (s, 3H, SiMe₂), 0.75 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 0.79 (s, 3H, SiMe₂), 1.07 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.13 (d, J_{HH} = 6.6 Hz, 6H, CH_{3iPr-NiPr}), 1.16 (d, J_{HH} = 6.6 Hz, 6H, CH_{3iPr-NiPr}), 1.19 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.24 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.28 (s, 9H, CH_{3tBu}), 1.45 (overlapped, 1H, CH_{2Norb}), 1.48 (s, 9H, CH_{3tBu}), 1.61 (d, J_{HH} = 8.0 Hz, 1H, CH_{2Norb}), 1.84 (m, 4H, CH_{2Norb}), 2.71 (br s, 1H, CH_{bridgehead}), 2.94 (sept, J_{HH} = 6.8 Hz, 1H, CH_{iPr-Dip}), 3.27 (sept, J_{HH} = 6.8 Hz, 1H, CH_{iPr-Dip}), 3.39 (br s, 1H, CH_{bridgehead}), 3.63 (dsept, J_{HP} = 5.2 Hz, J_{HH} = 6.8 Hz, 2H, CH_{iPr-NiPr}), 7.29-7.42 (m, 5H, CH_{Ar}), 7.47-7.52 (m, 2H, CH_{Ar}), 7.60-7.63 (m, 2H, CH_{Ar}), 7.68 (s, 4H, *p*-CH_{BAr}), 7.74-7.81 (m, 4H, CH_{Ar}), 7.96 (s, 8H, *m*-CH_{BAr}). ¹³C{¹H} NMR (100 MHz, -30 °C, THF-*d*₈): δ = 3.8 (d, J_{CP} = 1.9 Hz, SiMe₂), 6.4 (d, J_{CP} = 2.7 Hz, SiMe₂), 8.2 (d, J_{CP} = 8.0 and 125.1 Hz, Si-C-P), 23.2 (CH_{3iPr-NiPr}), 23.6 (CH_{3iPr-NiPr}), 24.5 (CH_{3iPr-Dip}), 24.8 (CH_{3iPr-Dip}), 25.6 (CH_{3iPr-Dip}), 26.0 (CH_{3iPr-Dip}), 27.2 (CH_{2Norb}), 28.4 (CH_{iPr-Dip}), 28.5 (CH_{2Norb}), 29.0 (CH_{iPr-Dip}), 33.1 (d, J_{CP} = 4.3 Hz, CH_{3tBu}), 33.4 (d, J_{CP} = 3.3 Hz, CH_{3tBu}), 42.0 (d, J_{CP} = 3.8 Hz, CH_{bridgehead}), 44.8 (d, J_{CP} = 12.3 Hz, CH_{bridgehead}), 47.6 (d, J_{CP} = 5.4 Hz, CH_{2Norb}), 51.0 (CH_{iPr-NiPr}), 52.5 (d, J_{CP} = 2.7 Hz, C_{tBu}), 52.9 (C_{tBu}), 101.9 (dd, J_{CP} = 41.8 and 2.7 Hz, NC=C_P), 118.2 (br s, *p*-CH_{BAr}), 123.7 (d, J_{CP} = 109.8 Hz, P-C_{Ar}), 123.7 (d, J_{CP} = 115.7 Hz, P-C_{Ar}), 125.3 (q, J_{CF} = 272.4 Hz, CF₃), 125.4 (CH_{Ar-Dip}), 126.2 (CH_{Ar-Dip}), 128.9 (CH_{Ar-Dip}), 129.9 (qq, J_{CF} = 31.8 Hz, J_{CB} = 3.2 Hz, *m*-C_{BAr}), 130.7 (d, J_{CP} = 15.0 Hz, CH_{Ar-PPh}), 130.8 (d, J_{CP} = 15.0 Hz, CH_{Ar-PPh}), 134.3 (d, J_{CP} = 10.9 Hz, CH_{Ar-PPh}), 134.7 (d, J_{CP} = 13.2 Hz, CH_{Ar-PPh}), 135.4 (o-CH_{BAr}), 135.4 (CH_{Ar-PPh}), 135.5 (CH_{Ar-PPh}), 137.7 (d, J_{CP} = 5.2 Hz, N-C_{Ar}), 147.7 (iPr-C_{Ar}), 148.5 (iPr-C_{Ar}), 162.8 (q, J_{CB} = 49.8 Hz, *isop*-C_{BAr}), 164.8 (dd, J_{CP} = 14.4 and 8.2 Hz, C=C_{Me₂}), 182.0 (d, J_{CP} = 37.7 Hz, NC=C_P). ³¹P{¹H} NMR (162 MHz, -30 °C, THF-*d*₈): δ = 44.1 (d, J_{PP} = 56.2 Hz, ⁺PPH₂), 68.6 (d, J_{PP} = 56.7 Hz, Si-P). ²⁹Si{¹H} NMR (79

MHz, -30 °C, THF-*d*₈): δ = 13.2 (d, J_{CP} = 2.9 Hz, SiMe₂), -38.5 (dd, J_{SiP} = 199.5 and 82.6 Hz, N-Si-P). ¹B{¹H} (128 MHz, -30 °C, THF-*d*₈): δ = -6.4 (BAr). ¹⁹F{¹H} (282 MHz, 25 °C, THF-*d*₈): δ = -63.3 (CF₃). IR(THF): ν = 2082.70 cm⁻¹ (C=O). Minor: 47%: ¹H NMR (400 MHz, -30 °C, THF-*d*₈): δ = 0.68 (s, 3H, SiMe₂), 0.74 (s, 3H, SiMe₂), 0.84 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.07 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.13 (d, J_{HH} = 6.6 Hz, 6H, CH_{3iPr-NiPr}), 1.16 (d, J_{HH} = 6.6 Hz, 6H, CH_{3iPr-NiPr}), 1.19 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.24 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.37 (s, 9H, CH_{3tBu}), 1.42 (s, 9H, CH_{3tBu}), 1.45 (overlapped, 1H, CH_{2Norb}), 1.48 (m, 2H, CH_{2Norb}), 1.66 (m, 2H, CH_{2Norb}), 1.80 (d, J_{HH} = 7.5 Hz, 1H, CH_{2Norb}), 2.48 (br s, 1H, CH_{bridgehead}), 2.73 (overlapped, 1H, CH_{iPr-Dip}), 3.36 (br s, 1H, CH_{bridgehead}), 3.52 (sept, J_{HH} = 6.8 Hz, 1H, CH_{iPr-Dip}), 3.66 (dsept, J_{HP} = 5.2 Hz, J_{HH} = 6.8 Hz, 2H, CH_{iPr-NiPr}). ¹³C{¹H} NMR (100 MHz, -30 °C, THF-*d*₈): δ = 4.2 (d, J_{CP} = 1.6 Hz, SiMe₂), 6.0 (d, J_{CP} = 2.7 Hz, SiMe₂), 8.2 (d, J_{CP} = 7.4 and 126.6 Hz, Si-C-P), 23.2 (CH_{3iPr-NiPr}), 23.7 (CH_{3iPr-NiPr}), 24.7 (CH_{3iPr-Dip}), 24.8 (CH_{3iPr-Dip}), 25.6 (CH_{3iPr-Dip}), 26.0 (CH_{3iPr-Dip}), 28.1 (CH_{iPr-Dip}), 28.8 (CH_{2Norb}), 29.3 (CH_{iPr-Dip}), 33.2 (d, J_{CP} = 4.9 Hz, CH_{3tBu}), 33.4 (d, J_{CP} = 3.3 Hz, CH_{3tBu}), 42.0 (d, J_{CP} = 3.0 Hz, CH_{bridgehead}), 44.3 (d, J_{CP} = 12.7 Hz, CH_{bridgehead}), 50.4 (CH_{2Norb}), 51.0 (CH_{iPr-NiPr}), 52.1 (d, J_{CP} = 2.7 Hz, C_{tBu}), 53.2 (C_{tBu}), 104.8 (dd, J_{CP} = 39.5 and 1.8 Hz, NC=C_P), 123.2 (d, J_{CP} = 115.5 Hz, P-C_{Ar}), 123.8 (d, J_{CP} = 110.0 Hz, P-C_{Ar}), 125.5 (CH_{Ar-Dip}), 126.3 (CH_{Ar-Dip}), 128.9 (CH_{Ar-Dip}), 130.5 (d, J_{CP} = 12.2 Hz, CH_{Ar-PPh}), 130.6 (d, J_{CP} = 11.9 Hz, CH_{Ar-PPh}), 134.3 (d, J_{CP} = 12.0 Hz, CH_{Ar-PPh}), 134.6 (d, J_{CP} = 10.8 Hz, CH_{Ar-PPh}), 137.9 (d, J_{CP} = 7.4 Hz, N-C_{Ar}), 145.5 (iPr-C_{Ar}), 147.5 (iPr-C_{Ar}), 166.5 (dd, J_{CP} = 15.4 and 10.2 Hz, C=C=O), 182.5 (d, J_{CP} = 34.5 Hz, NC=C_P). ³¹P{¹H} NMR (162 MHz, -30 °C, THF-*d*₈): δ = 43.6 (d, J_{PP} = 51.8 Hz, ⁺PPH₂), 65.9 (d, J_{PP} = 52.8 Hz, Si-P). ²⁹Si{¹H} NMR (79 MHz, -30 °C, THF-*d*₈): δ = 12.6 (d, J_{CP} = 3.9 Hz, SiMe₂), -25.5 (dd, J_{SiP} = 208.8 and 79.7 Hz, N-Si-P).

Synthesis of 9: In an NMR tube, to a THF (0.4 ml) solution of **3** (100 mg, 0.065 mmol) was added H₂O solution in THF (0.1 M, 0.6 mL, 0.06 mmol) at -30 °C. All volatiles were removed under reduced pressure. **9** was obtained as colorless crystals (60 mg, 60%) in a saturated Et₂O solution at -30 °C. Crystals suitable for X-ray diffraction analysis were grown from saturated C₆H₅F/pentane solution at -30 °C. Mp. 151-155 °C (decomp.). Major: (88%): ¹H NMR (400 MHz, -30 °C, THF-*d*₈): δ = 0.68 (s, 3H, SiMe₂), 0.75 (s, 3H, SiMe₂), 0.81 (dd, J_{HP} = 15.4 and 2.8 Hz, 1H, Si-OH), 0.95 (d, J_{HH} = 6.8 Hz, 6H, CH_{3iPr-NiPr}), 1.06 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.07 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.11 (d, J_{HH} = 6.5 Hz, 6H, CH_{3iPr-NiPr}), 1.19 (d, J_{HH} = 6.5 Hz, 6H, CH_{3iPr-Dip}), 1.29 (s, 18H, CH_{3tBu}), 1.32 (m, 1H, CH_{2Norb}), 1.40 (d, J_{HH} = 6.5 Hz, 6H, CH_{3iPr-Dip}), 1.46 (d, J_{HH} = 8.0 Hz, 1H, CH_{2Norb}), 1.66 (d, J_{HH} = 8.0 Hz, 1H, CH_{2Norb}), 1.67 (overlapped, 1H, CH_{2Norb}), 1.83 (m, 2H, CH_{2Norb}), 2.65 (m, 1H, CH_{bridgehead}), 3.23 (sept, J_{HH} = 6.8 Hz, 1H, CH_{iPr-Dip}), 3.30 (overlapped, 1H, CH_{iPr-Dip}), 3.30 (m, 1H, CH_{bridgehead}), 3.42 (dsept, J_{HP} = 13.7 Hz, J_{HH} = 6.8 Hz, 2H, CH_{iPr-NiPr}), 5.64 (d, J_{HP} = 12.7 Hz, 1H, Si-C-H), 7.30-7.43 (m, 7H, CH_{Ar}), 7.47-7.61 (m, 4H, CH_{Ar}), 7.65 (s, 4H, *p*-CH_{BAr}), 7.69-7.74 (m, 2H, CH_{Ar}), 7.86 (s, 8H, *m*-CH_{BAr}). ¹³C{¹H} NMR (100 MHz, -30 °C, THF-*d*₈): δ = 4.1 (d, J_{CP} = 2.7 Hz, SiMe₂), 5.8 (d, J_{CP} = 2.3 Hz, SiMe₂), 10.6 (dd, J_{CP} = 120.1 and 36.1 Hz, Si-CH-P), 23.6 (CH_{3iPr-NiPr}), 23.9 (CH_{3iPr-NiPr}), 24.8 (CH_{iPr-Dip}), 25.0 (CH_{3iPr-Dip}), 25.4 (CH_{3iPr-Dip}), 25.8 (CH_{3iPr-Dip}), 25.9 (CH_{2Norb}), 28.4 (CH_{2Norb}), 28.9 (2xCH_{iPr-Dip}), 32.1 (d, J_{CP} = 5.0 Hz, CH_{3tBu}), 32.8 (d, J_{CP} = 5.0 Hz, CH_{3tBu}), 41.5 (d, J_{CP} = 1.7 Hz, CH_{bridgehead}), 45.2 (d, J_{CP} = 8.2 Hz, CH_{bridgehead}), 47.8 (d, J_{CP} = 5.9 Hz, CH_{2Norb}), 48.3 (d, J_{CP} = 5.9 Hz, CH_{iPr-NiPr}), 52.8 (C_{tBu}), 53.0 (C_{tBu}), 97.5 (d, J_{CP} = 57.7 Hz,

NC=CP), 118.2 (br sept, $J_{CF} = 3.9$ Hz, p -CH_{BAr}), 125.4 (CH_{Ar-Dip}), 125.4 (q, $J_{CF} = 272.3$ Hz, CF₃), 125.6 (CH_{Ar-Dip}), 128.9 (CH_{Ar-Dip}), 129.1 (d, $J_{CP} = 12.3$ Hz, CH_{Ar-PPh}), 129.8 (d, $J_{CP} = 12.5$ Hz, CH_{Ar-PPh}), 129.9 (qq, $J_{CF} = 31.5$ Hz, $J_{CB} = 2.9$ Hz, m -C_{BAr}), 131.0 (d, $J_{CP} = 141.8$ Hz, P-C_{Ar}), 132.0 (d, $J_{CP} = 3.1$ Hz, CH_{Ar-PPh}), 132.2 (d, $J_{CP} = 10.0$ Hz, CH_{Ar-PPh}), 132.7 (d, $J_{CP} = 3.2$ Hz, CH_{Ar-PPh}), 132.9 (d, $J_{CP} = 107.9$ Hz, P-C_{Ar}), 133.6 (d, $J_{CP} = 11.3$ Hz, CH_{Ar-PPh}), 135.4 (o-CH_{BAr}), 135.5 (d, $J_{CP} = 4.5$ Hz, N-C_{Ar}), 147.4 (iPr-C_{Ar}), 147.8 (iPr-C_{Ar}), 162.7 (q, $J_{CB} = 49.5$ Hz, *isop*-C_{BAr}), 188.0 (d, $J_{CP} = 24.5$ Hz, NC=CP). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, -30 °C, THF- d_8): $\delta = 35.0$ (d, $J_{PP} = 9.0$ Hz, Si-P), 42.2 (d, $J_{PP} = 9.0$ Hz, $^+\text{PPh}_2$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, -30 °C, THF- d_8): $\delta = 20.2$ (d, $J_{CP} = 4.4$ Hz, SiMe₂), -29.2 (dd, $J_{SiP} = 196.1$ and 28.9 Hz, N-Si-P). $^{11}\text{B}\{^1\text{H}\}$ (128 MHz, -30 °C, THF- d_8): $\delta = -6.5$ (BAR). $^{19}\text{F}\{^1\text{H}\}$ (282 MHz, 25 °C, THF- d_8): $\delta = -63.3$ (CF₃). Minor (12%): $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, -30 °C, THF- d_8): $\delta = 4.0$ (d, $J_{CP} = 2.3$ Hz, SiMe₂), 6.0 (d, $J_{CP} = 1.5$ Hz, SiMe₂), 11.8 (d, $J_{CP} = 65.4$ Hz, Si-CH-P), 22.7 (CH_{3iPr-NiPr}), 23.7 (CH_{3iPr-NiPr}), 24.3 (CH_{iPr-Dip}), 25.2 (CH_{3iPr-Dip}), 25.6 (CH_{3iPr-Dip}), 26.7 (CH_{3iPr-Dip}), 28.5 (2xCH_{iPr-Dip}), 32.3 (d, $J_{CP} = 5.1$ Hz, CH_{3tBu}), 32.8 (d, $J_{CP} = 4.8$ Hz, CH_{3tBu}), 41.0 (d, $J_{CP} = 1.9$ Hz, CH_{bridgehead}), 44.8 (d, $J_{CP} = 8.6$ Hz, CH_{bridgehead}), 50.4 (d, $J_{CP} = 2.3$ Hz, CH_{iPr-NiPr}), 52.7 (C_{tBu}), 53.1 (C_{tBu}), 98.4 (d, $J_{CP} = 59.0$ Hz, NC=CP), 125.3 (CH_{Ar-Dip}), 125.5 (CH_{Ar-Dip}), 134.0 (d, $J_{CP} = 4.6$ Hz, N-C_{Ar}), 147.9 (iPr-C_{Ar}), 148.0 (iPr-C_{Ar}), 187.3 (d, $J_{CP} = 24.5$ Hz, NC=CP). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, -30 °C, THF- d_8): $\delta = 36.1$ (br s, Si-P), 44.80 (br s, $^+\text{PPh}_2$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (59 MHz, -30 °C, THF- d_8): $\delta = 19.9$ (d, $J_{CP} = 3.9$ Hz, SiMe₂), -28.1 (dd, $J_{SiP} = 200.4$ and 28.3 Hz, N-Si-P).

Synthesis of 10: A C₆H₅F (0.4 ml) solution of **3** (85 mg, 0.050 mmol) was added TMSN₃ (0.1 mL, 0.76 mmol) at room temperature. After 12 hours, all volatiles were removed under vacuum. **10** was obtained as colorless crystals in C₆H₅F/toluene at -30 °C (82 mg, 91%). Crystals suitable for X-ray diffraction analysis were grown from saturated CH₂Cl₂/pentane solution at -30 °C. Mp. 137-140 °C (decomp.). ^1H NMR (400 MHz, -30 °C, CD₂Cl₂): $\delta = -1.11$ (s, 9H, SiMe₃), 0.70 (s, 3H, SiMe₂), 0.72 (br s, 6H, CH_{3iPr-NiPr}), 0.75 (s, 3H, SiMe₂), 1.01 (d, $J_{HH} = 6.8$ Hz, 3H, CH_{3iPr-Dip}), 1.08 (d, $J_{HH} = 6.8$ Hz, 6H, CH_{3iPr-Dip}), 1.19 (d, $J_{HH} = 6.8$ Hz, 3H, CH_{3iPr-Dip}), 1.35 (d, $J_{HH} = 6.8$ Hz, 6H, CH_{3iPr-NiPr}), 1.37 (s, 9H, CH_{3tBu}), 1.39 (overlapped, 1H, CH_{2Norb}), 1.43 (m, 1H, CH_{2Norb}), 1.56 (s, 9H, CH_{3tBu}), 1.56 (overlapped, 1H, CH_{2Norb}), 1.70 (m, 2H, CH_{2Norb}), 1.83 (m, 1H, CH_{2Norb}), 2.77 (m, 1H, CH_{bridgehead}), 3.16 (m, 3H, CH_{iPr-Dip} and CH_{iPr-NiPr}), 3.30 (m, 1H, CH_{bridgehead}), 4.04 (sept, $J_{HH} = 6.9$ Hz, 1H, CH_{iPr-Dip}), 7.12 (br s, 2H, CH_{Ar}), 7.37-7.56 (m, 6H, CH_{Ar}), 7.65-7.70 (m, 3H, CH_{Ar}), 7.77 (s, 4H, p -CH_{BAr}), 7.86 (s, 8H, m -CH_{BAr}), 8.37 (dd, $J_{HH} = 14.0$ and 7.9 Hz, 2H, CH_{Ar}). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, -30 °C, CD₂Cl₂): $\delta = 4.3$ (SiMe₃), 4.9 (SiMe₂), 7.0 (SiMe₂), 23.7 (br s, CH_{3iPr-NiPr}), 23.9 (CH_{3iPr-NiPr}), 24.4 (2xCH_{3iPr-Dip}), 24.9 (CH_{2Norb}), 25.4 (CH_{3iPr-Dip}), 25.8 (CH_{3iPr-Dip}), 27.2 (dd, $J_{CP} = 82.0$ and 29.5 Hz, C=N=N), 27.5 (CH_{2Norb}), 27.6 (CH_{iPr-Dip}), 28.0 (CH_{iPr-Dip}), 32.9 (d, $J_{CP} = 5.0$ Hz, CH_{3tBu}), 33.6 (d, $J_{CP} = 5.0$ Hz, CH_{3tBu}), 41.5 (d, $J_{CP} = 3.2$ Hz, CH_{bridgehead}), 45.8 (d, $J_{CP} = 9.1$ Hz, CH_{bridgehead}), 47.2 (d, $J_{CP} = 8.2$ Hz, CH_{2Norb}), 51.0 (br s, CH_{iPr-NiPr}), 52.6 (C_{tBu}), 52.9 (C_{tBu}), 98.5 (d, $J_{CP} = 50.4$ Hz, NC=CP), 117.6 (br s, p -CH_{BAr}), 121.1 (d, $J_{CP} = 116.4$ Hz, P-C_{Ar}), 122.7 (d, $J_{CP} = 114.0$ Hz, P-C_{Ar}), 124.6 (q, $J_{CF} = 272.6$ Hz, CF₃), 125.7 (CH_{Ar-Dip}), 126.4 (CH_{Ar-Dip}), 128.5 (CH_{Ar-Dip}), 128.9 (qq, $J_{CF} = 31.3$ Hz, $J_{CB} = 3.2$ Hz, m -C_{BAr}), 129.2 (d, $J_{CP} = 13.4$ Hz, 2xCH_{Ar-PPh}), 130.2 (d, $J_{CP} = 13.6$ Hz, 2xCH_{Ar-PPh}), 134.9 (o-CH_{BAr}), 137.7 (d, $J_{CP} = 3.2$ Hz, CH_{Ar-PPh}), 137.1 (d, $J_{CP} = 4.5$ Hz, N-C_{Ar}), 146.4 (iPr-C_{Ar}), 148.1 (iPr-C_{Ar}), 161.9 (q, $J_{CB} = 49.5$ Hz, *isop*-C_{BAr}), 188.6 (d, $J_{CP} = 25.9$

Hz, NC=CP). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, -30 °C, CD₂Cl₂): $\delta = 31.7$ (d, $J_{PP} = 7.8$ Hz, Si-P), 57.9 (br s, $^+\text{PPh}_2$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, -30 °C, CD₂Cl₂): $\delta = 18.1$ (d, $J_{CP} = 2.5$ Hz, SiMe₂), -20.7 (d, $J_{CP} = 2.5$ Hz, SiMe₂), -76.4 (d, $J_{SiP} = 180.6$ and 11.9 Hz, N-Si-P). $^{11}\text{B}\{^1\text{H}\}$ (128 MHz, -30 °C, CD₂Cl₂): $\delta = -6.6$ (BAR). $^{19}\text{F}\{^1\text{H}\}$ (282 MHz, 25 °C, CD₂Cl₂): $\delta = -62.8$ (CF₃). IR(THF): $\nu = 2073.26$ cm⁻¹ (C=N=N).

Synthesis of 11: A THF (0.4 ml) solution of **3** (200 mg, 0.12 mmol) was added benzaldehyde (12 μL , 0.12 mmol) at room temperature. After 30 min, all volatiles were removed under vacuum. **11** was obtained as yellow crystals in THF/pentane solution at -30 °C (55 mg, 28%) as yellow crystals. Crystals suitable for X-ray diffraction analysis were grown from saturated THF/pentane solution at -30 °C. Mp. 98-100 °C (decomp.). Major (53%): ^1H NMR (400 MHz, -30 °C, THF- d_8): $\delta = 0.74$ (s, 3H, SiMe₂), 0.85 (s, 3H, SiMe₂), 0.86 (d, $J_{HH} = 6.6$ Hz, 6H, CH_{3iPr-NiPr}), 0.91 (d, $J_{HH} = 6.6$ Hz, 6H, CH_{3iPr-NiPr}), 1.13 (d, $J_{HH} = 6.8$ Hz, 3H, CH_{3iPr-Dip}), 1.18 (s, 9H, CH_{3tBu}), 1.20 (d, $J_{HH} = 6.8$ Hz, 3H, CH_{3iPr-Dip}), 1.22 (s, 9H, CH_{3tBu}), 1.32 (d, $J_{HH} = 6.8$ Hz, 3H, CH_{3iPr-Dip}), 1.38 (d, $J_{HH} = 6.8$ Hz, 3H, CH_{3iPr-Dip}), 1.53 (d, $J_{CP} = 7.8$ Hz, 1H, CH_{2Norb}), 1.65 (m, 1H, CH_{2Norb}), 1.70 (m, 1H, CH_{2Norb}), 1.76 (m, 1H, CH_{2Norb}), 1.94 (m, 1H, CH_{2Norb}), 2.05 (m, 1H, CH_{2Norb}), 2.79 (overlapped, 1H, CH_{bridgehead}), 3.30 (sept, $J_{HH} = 6.8$ Hz, 1H, CH_{iPr-Dip}), 3.43 (overlapped, 1H, CH_{bridgehead}), 3.60 (overlapped, 1H, CH_{iPr-Dip}), 3.73 (m, 2H, CH_{iPr-NiPr}), 5.66 (dd, $J_{HP} = 18.3$ and 3.0 Hz, 1H, O-CH), 6.88-7.22 (m, 12H, CH_{Ar}), 7.43-7.54 (m, 7H, CH_{Ar}), 7.61-7.64 (m, 4H, CH_{Ar}), 7.64 (s, 4H, p -CH_{BAr}), 7.85 (s, 8H, m -CH_{BAr}). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, -30 °C, THF- d_8): $\delta = 3.8$ (d, $J_{CP} = 2.3$ Hz, SiMe₂), 5.9 (SiMe₂), 23.3 (d, $J_{CP} = 5.0$ Hz, CH_{3iPr-NiPr}), 24.7 (CH_{3iPr-Dip}), 25.2 (CH_{2Norb}), 25.4 (CH_{3iPr-NiPr}), 25.5 (CH_{3iPr-Dip}), 26.0 (CH_{3iPr-Dip}), 27.8 (CH_{2Norb}), 28.7 (CH_{3iPr-Dip}), 29.2 (CH_{iPr-Dip}), 29.6 (CH_{iPr-Dip}), 32.3 (d, $J_{CP} = 5.4$ Hz, CH_{3tBu}), 32.7 (d, $J_{CP} = 5.9$ Hz, CH_{3tBu}), 41.5 (CH_{bridgehead}), 46.3 (d, $J_{CP} = 9.1$ Hz, CH_{bridgehead}), 47.8 (d, $J_{CP} = 5.5$ Hz, CH_{2Norb}), 48.1 (d, $J_{CP} = 7.3$ Hz, CH_{iPr-NiPr}), 52.7 (C_{tBu}), 53.7 (C_{tBu}), 86.8 (d, $J_{CP} = 3.2$ Hz, O-CH), 100.4 (d, $J_{CP} = 59.8$ Hz, NC=CP), 118.1 (br sept, $J_{CF} = 3.9$ Hz, p -CH_{BAr}), 125.3 (q, $J_{CF} = 272.5$ Hz, CF₃), 125.7 (d, $J_{CP} = 110.2$ Hz, P-C_{Ar}), 126.2 (CH_{Ar-Dip}), 126.6 (CH_{Ar-Dip}), 127.6 (CH_{Ar-CPh}), 127.9 (d, $J_{CP} = 114.2$ Hz, P-C_{Ar}), 128.2 (CH_{Ar-CPh}), 128.3 (CH_{Ar-CPh}), 129.0 (d, $J_{CP} = 12.6$ Hz, CH_{Ar-PPh}), 129.8 (CH_{Ar-Dip}), 129.8 (qq, $J_{CF} = 31.5$ Hz, $J_{CB} = 2.7$ Hz, m -C_{BAr}), 132.3 (d, $J_{CP} = 3.2$ Hz, CH_{Ar-PPh}), 132.6 (d, $J_{CP} = 10.2$ Hz, CH_{Ar-PPh}), 132.9 (d, $J_{CP} = 9.3$ Hz, CH_{Ar-PPh}), 133.0 (d, $J_{CP} = 3.7$ Hz, CH_{Ar-PPh}), 133.4 (d, $J_{CP} = 10.4$ Hz, CH_{Ar-PPh}), 135.1 (d, $J_{CP} = 5.0$ Hz, N-C_{Ar}), 135.4 (o-CH_{BAr}), 144.6 (C_{Ar-CPh}), 146.9 (iPr-C_{Ar}), 148.4 (iPr-C_{Ar}), 162.7 (q, $J_{CB} = 49.8$ Hz, *isop*-C_{BAr}), 188.9 (d, $J_{CP} = 25.6$ Hz, NC=CP). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, -30 °C, THF- d_8): $\delta = 24.8$ (d, $J_{PP} = 5.2$ Hz, Si-satellite: $J_{PSi} = 163.2$ Hz, Si-P), 32.3 (d, $J_{PP} = 5.2$ Hz, $^+\text{PPh}_2$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, -30 °C, THF- d_8): $\delta = 23.4$ (d, $J_{CP} = 3.9$ Hz, SiMe₂), -31.2 (dd, $J_{SiP} = 162.9$ and 16.6 Hz, N-Si-P). $^{11}\text{B}\{^1\text{H}\}$ (128 MHz, -30 °C, THF- d_8): $\delta = -6.5$ (BAR). $^{19}\text{F}\{^1\text{H}\}$ (282 MHz, 25 °C, THF- d_8): $\delta = -63.3$ (CF₃). Minor: (47%): ^1H NMR (400 MHz, -30 °C, THF- d_8): $\delta = 0.74$ (s, 3H, SiMe₂), 0.88 (s, 3H, SiMe₂), 0.89 (d, $J_{HH} = 6.6$ Hz, 6H, CH_{3iPr-NiPr}), 1.05 (d, $J_{HH} = 6.8$ Hz, 3H, CH_{3iPr-Dip}), 1.07 (d, $J_{HH} = 6.6$ Hz, 6H, CH_{3iPr-NiPr}), 1.14 (s, 9H, CH_{3tBu}), 1.31 (d, $J_{HH} = 6.8$ Hz, 3H, CH_{3iPr-Dip}), 1.32 (s, 9H, CH_{3tBu}), 1.32 (d, $J_{HH} = 6.8$ Hz, 3H, CH_{3iPr-Dip}), 1.40 (d, $J_{HH} = 6.8$ Hz, 3H, CH_{3iPr-Dip}), 1.57 (d, $J_{CP} = 8.1$ Hz, 1H, CH_{2Norb}), 1.76 (m, 1H, CH_{2Norb}), 2.79 (overlapped, 1H, CH_{bridgehead}), 3.41 (overlapped, 1H, CH_{iPr-Dip}), 3.44 (overlapped, 1H, CH_{bridgehead}), 3.60 (overlapped, 1H, CH_{iPr-Dip}), 3.73 (m, 2H, CH_{iPr-NiPr}), 5.51 (dd, $J_{HP} = 18.3$ and 2.5 Hz, 1H, O-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, -30 °C, THF- d_8): δ

= 3.6 (d, J_{CP} = 1.9 Hz, SiMe₂), 5.7 (SiMe₂), 23.5 (d, J_{CP} = 6.4 Hz, CH_{3iPr-NiPr}), 24.6 (CH_{3iPr-Dip}), 25.5 (CH_{3iPr-NiPr}), 26.0 (CH_{3iPr-Dip}), 27.1 (CH_{2Norb}), 27.3 (CH_{3iPr-Dip}), 27.9 (CH_{2Norb}), 28.9 (CH_{iPr-Dip}), 29.0 (CH_{iPr-Dip}), 31.6 (d, J_{CP} = 5.4 Hz, CH_{3tBu}), 32.7 (d, J_{CP} = 5.9 Hz, CH_{3tBu}), 42.2 (CH_{bridgehead}), 45.9 (d, J_{CP} = 8.6 Hz, CH_{bridgehead}), 47.9 (d, J_{CP} = 7.3 Hz, CH_{iPr-NiPr}), 48.3 (d, J_{CP} = 5.9 Hz, CH_{2Norb}), 52.4 (C_{tBu}), 53.8 (C_{tBu}), 86.6 (d, J_{CP} = 2.7 Hz, O-CH), 100.7 (d, J_{CP} = 60.3 Hz, NC=C_P), 126.3 (CH_{Ar-Dip}), 126.4 (CH_{Ar-Dip}), 127.8 (CH_{Ar-CPh}), 128.1 (CH_{Ar-CPh}), 128.2 (CH_{Ar-CPh}), 128.9 (d, J_{CP} = 12.7 Hz, CH_{Ar-PPh}), 130.1 (CH_{Ar-Dip}), 132.0 (d, J_{CP} = 3.2 Hz, CH_{Ar-PPh}), 132.7 (d, J_{CP} = 2.7 Hz, CH_{Ar-PPh}), 133.1 (d, J_{CP} = 10.4 Hz, CH_{Ar-PPh}), 133.9 (d, J_{CP} = 5.0 Hz, N-C_{Ar}), 143.5 (C_{Ar-CPh}), 147.6 (iPr-C_{Ar}), 149.4 (iPr-C_{Ar}), 189.6 (d, J_{CP} = 23.2 Hz, NC=C_P). ³¹P{¹H} NMR (162 MHz, -30 °C, THF-*d*₈): δ = 24.0 (d, J_{PP} = 4.5 Hz, Si-satellite: J_{PSi} = 158.9 Hz, Si-P), 31.8 (br s, ¹PPh₂). ²⁹Si{¹H} NMR (79 MHz, -30 °C, THF-*d*₈): δ = 22.8 (d, J_{CP} = 3.4 Hz, SiMe₂), -29.5 (dd, J_{SiP} = 158.7 and 18.4 Hz, N-Si-P).

Synthesis of 12: A THF (0.4 ml) solution of **11** (55 mg, 0.30 mmol) was kept at 25 °C and monitored by NMR. After 2 days, all volatiles were removed under reduced pressure and the residues were crystallized from THF/pentane solution at -30 °C to obtain **12** as yellow crystals (13 mg, 24%). Major: (60%): ¹H NMR (500 MHz, 25 °C, THF-*d*₈): δ = 0.56 (s, 3H, SiMe₂), 0.64 (s, 3H, SiMe₂), 0.66 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.18 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.20 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.23 (s, 9H, CH_{3tBu}), 1.34 (d, J_{HH} = 6.8 Hz, 6H, CH_{3iPr-NiPr}), 1.41 (d, J_{HH} = 6.8 Hz, 6H, CH_{3iPr-NiPr}), 1.48 (d, J_{CP} = 8.8 Hz, 1H, CH_{2Norb}), 1.54 (m, 1H, CH_{2Norb}), 1.61 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.69 (s, 9H, CH_{3tBu}), 1.69 (overlapped, 1H, CH_{2Norb}), 1.77 (m, 2H, CH_{2Norb}), 1.91 (m, 1H, CH_{2Norb}), 2.81 (m, 1H, CH_{bridgehead}), 3.22 (sept, J_{HH} = 6.8 Hz, 1H, CH_{iPr-Dip}), 3.50 (m, 1H, CH_{bridgehead}), 3.84 (dsept, J_{HP} = 13.7 Hz, J_{HH} = 6.8 Hz, 2H, CH_{iPr-NiPr}), 4.00 (sept, J_{HH} = 6.8 Hz, 1H, CH_{iPr-Dip}), 6.83-6.98 (m, 3H, CH_{Ar}), 7.04 (td, J_{HP} = 7.5 Hz, J_{HH} = 3.7 Hz, 2H, CH_{Ar}), 7.08 (dd, J_{HH} = 7.8 and 1.7 Hz, 1H, CH_{Ar}), 7.11-7.17 (m, 3H, CH_{Ar}), 7.42 (dd, J_{HH} = 7.8 and 1.7 Hz, 1H, CH_{Ar}), 7.28-7.35 (m, 3H, CH_{Ar}), 7.58 (s, 4H, *p*-CH_{BAr}), 7.60-7.63 (m, 1H, CH_{Ar}), 7.80 (s, 8H, *m*-CH_{BAr}), 7.86 (dd, J_{HP} = 13.0 Hz, J_{HH} = 8.6 Hz, 2H, CH_{Ar}), 8.08 (dd, J_{HP} = 13.1 Hz, J_{HH} = 7.2 Hz, 2H, CH_{Ar}), 8.86 (d, J_{HP} = 58.6 Hz, 1H, P-C=CH). ¹³C{¹H} NMR (125 MHz, 25 °C, THF-*d*₈): δ = 4.0 (d, J_{CP} = 1.3 Hz, SiMe₂), 6.8 (d, J_{CP} = 1.8 Hz, SiMe₂), 24.1 (d, J_{CP} = 3.5 Hz, CH_{3iPr-NiPr}), 24.4 (CH_{3iPr-Dip}), 24.6 (d, J_{CP} = 2.9 Hz, CH_{3iPr-NiPr}), 25.4 (CH_{3iPr-Dip}), 25.5 (CH_{2Norb}), 26.3 (CH_{3iPr-Dip}), 26.8 (CH_{3iPr-Dip}), 28.0 (CH_{2Norb}), 29.0 (CH_{iPr-Dip}), 29.1 (CH_{iPr-Dip}), 33.1 (d, J_{CP} = 5.2 Hz, CH_{3tBu}), 33.3 (d, J_{CP} = 4.6 Hz, CH_{3tBu}), 42.0 (d, J_{CP} = 2.3 Hz, CH_{bridgehead}), 45.8 (d, J_{CP} = 8.7 Hz, CH_{bridgehead}), 47.9 (d, J_{CP} = 8.1 Hz, CH_{2Norb}), 52.7 (d, J_{CP} = 5.8 Hz, CH_{iPr-NiPr}), 52.8 (C_{tBu}), 54.0 (C_{tBu}), 100.9 (d, J_{CP} = 71.1 Hz, NC=C_P), 118.0 (br sept, J_{CF} = 4.0 Hz, *p*-CH_{BAr}), 125.3 (q, J_{CF} = 272.3 Hz, CF₃), 125.3 (CH_{Ar-Dip}), 125.9 (d, J_{CP} = 98.9 Hz, P-C_{Ar}), 126.6 (d, J_{CP} = 96.5 Hz, P-C_{Ar}), 126.8 (CH_{Ar-Dip}), 127.3 (dd, J_{CP} = 42.8 and 59.2 Hz, P-C=C), 128.2 (CH_{Ar-Dip}), 129.0 (CH_{Ar-CPh}), 129.2 (d, J_{CP} = 12.8 Hz, CH_{Ar-PPh}), 129.5 (d, J_{CP} = 13.4 Hz, CH_{Ar-PPh}), 129.9 (qq, J_{CF} = 31.2 Hz, J_{CB} = 2.6 Hz, *m*-C_{BAr}), 130.4 (CH_{Ar-CPh}), 130.9 (CH_{Ar-CPh}), 133.8 (d, J_{CP} = 9.2 Hz, C_{Ar-CPh}), 134.4 (d, J_{CP} = 3.5 Hz, CH_{Ar-PPh}), 134.7 (d, J_{CP} = 2.9 Hz, CH_{Ar-PPh}), 135.4 (o-CH_{BAr}), 135.9 (d, J_{CP} = 11.6 Hz, CH_{Ar-PPh}), 136.3 (d, J_{CP} = 11.6 Hz, CH_{Ar-PPh}), 136.6 (N-C_{Ar}), 147.3 (iPr-C_{Ar}), 149.6 (iPr-C_{Ar}), 162.2 (q, J_{CB} = 50.0 Hz, *isop*-C_{BAr}), 165.5 (C=C_H), 189.4 (d, J_{CP} = 27.2 Hz, NC=C_P). ³¹P{¹H} NMR (202 MHz, 25 °C, THF-*d*₈): δ = 38.5 (d, J_{PP} = 9.3 Hz, Si-P), 42.4 (d, J_{PP} = 9.3 Hz, ¹PPh₂). ²⁹Si{¹H} NMR (99 MHz, 25 °C,

THF-*d*₈): δ = 17.9 (d, J_{CP} = 4.2 Hz, SiMe₂), -50.5 (dd, J_{SiP} = 140.8 and 17.2 Hz, N-Si-P). ¹¹B{¹H} (160 MHz, 25 °C, THF-*d*₈): δ = -6.5 (BAr). ¹⁹F (470 MHz, 25 °C, THF-*d*₈): δ = -63.4 (CF₃). Minor (40): ¹H NMR (500 MHz, 25 °C, THF-*d*₈): δ = 0.40 (s, 3H, SiMe₂), 0.67 (s, 3H, SiMe₂), 0.59 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.01 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.10 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.20 (d, J_{HH} = 6.8 Hz, 6H, CH_{3iPr-NiPr}), 1.25 (s, 9H, CH_{3tBu}), 1.32 (d, J_{HH} = 6.8 Hz, 6H, CH_{3iPr-NiPr}), 1.59 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.69 (s, 9H, CH_{3tBu}), 1.82 (m, 3H, CH_{2Norb}), 1.92 (m, 2H, CH_{2Norb}), 2.70 (m, 1H, CH_{bridgehead}), 3.12 (sept, J_{HH} = 6.8 Hz, 1H, CH_{iPr-Dip}), 3.32 (m, 1H, CH_{bridgehead}), 3.70 (dsept, J_{HP} = 14.4 Hz, J_{HH} = 6.8 Hz, 2H, CH_{iPr-NiPr}), 3.85 (overlapped, 1H, CH_{iPr-Dip}), 8.76 (d, J_{HP} = 58.4 Hz, 1H, P-C=CH). ¹³C{¹H} NMR (125 MHz, 25 °C, THF-*d*₈): δ = 4.2 (d, J_{CP} = 1.9 Hz, SiMe₂), 6.7 (d, J_{CP} = 2.0 Hz, SiMe₂), 23.7 (d, J_{CP} = 4.0 Hz, CH_{3iPr-NiPr}), 24.4 (CH_{3iPr-Dip}), 24.7 (d, J_{CP} = 2.2 Hz, CH_{3iPr-NiPr}), 25.7 (CH_{3iPr-Dip}), 26.2 (CH_{3iPr-Dip}), 26.4 (CH_{3iPr-Dip}), 27.7 (CH_{2Norb}), 28.5 (CH_{2Norb}), 29.0 (CH_{iPr-Dip}), 30.0 (CH_{iPr-Dip}), 33.4 (d, J_{CP} = 4.4 Hz, CH_{3tBu}), 33.5 (d, J_{CP} = 3.7 Hz, CH_{3tBu}), 41.4 (d, J_{CP} = 2.3 Hz, CH_{bridgehead}), 45.8 (d, J_{CP} = 8.2 Hz, CH_{bridgehead}), 47.6 (d, J_{CP} = 4.0 Hz, CH_{2Norb}), 52.7 (d, J_{CP} = 5.8 Hz, CH_{iPr-NiPr}), 52.6 (C_{tBu}), 53.7 (C_{tBu}), 100.3 (d, J_{CP} = 72.0 Hz, NC=C_P), 124.8 (CH_{Ar-Dip}), 126.4 (CH_{Ar-Dip}), 128.2 (CH_{Ar-Dip}), 128.9 (CH_{Ar-CPh}), 129.7 (d, J_{CP} = 11.7 Hz, CH_{Ar-PPh}), 130.4 (CH_{Ar-CPh}), 130.9 (CH_{Ar-CPh}), 134.8 (d, J_{CP} = 10.4 Hz, CH_{Ar-PPh}), 135.1 (d, J_{CP} = 12.9 Hz, C_{Ar-CPh}), 138.2 (d, J_{CP} = 12.7 Hz, CH_{Ar-PPh}), 136.6 (N-C_{Ar}), 147.7 (iPr-C_{Ar}), 150.8 (iPr-C_{Ar}), 166.3 (C=C_H), 190.1 (d, J_{CP} = 26.6 Hz, NC=C_P). ³¹P{¹H} NMR (202 MHz, 25 °C, THF-*d*₈): δ = 35.3 (d, J_{PP} = 7.5 Hz, Si-P), 45.4 (d, J_{PP} = 7.5 Hz, ¹PPh₂). ²⁹Si{¹H} NMR (99 MHz, 25 °C, THF-*d*₈): δ = 17.6 (d, J_{CP} = 3.8 Hz, SiMe₂), -49.0 (dd, J_{SiP} = 133.2 and 18.4 Hz, N-Si-P).

Synthesis of 13: A THF (0.4 ml) solution of **11** (100 mg, 0.56 mmol) was heated at 60 °C. After 24 hours, all volatiles were removed under vacuum and the residues were crystallized from THF/pentane (0.1 + 0.4 mL) at -30 °C to obtain **13** (46 mg, 46%) as yellow crystals. Crystals suitable for X-ray diffraction analysis were grown from saturated THF/pentane solution at -30 °C. Mp. 205-206 °C (decomp.). ¹H NMR (300 MHz, 25 °C, THF-*d*₈): δ = 0.27 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 0.85 (s, 3H, SiMe₂), 0.86 (s, 3H, SiMe₂), 0.99 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.36 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr-Dip}), 1.43 (d, J_{HP} = 0.7 Hz, 9H, CH_{3tBu}), 1.44 (d, J_{HP} = 0.7 Hz, 9H, CH_{3tBu}), 1.44 (overlapped, 3H, CH_{3iPr-Dip}), 1.40 (m, 1H, CH_{2Norb}), 1.53 (m, 1H, CH_{2Norb}), 1.62 (m, 1H, CH_{2Norb}), 1.82 (m, 1H, CH_{2Norb}), 1.97 (m, 2H, CH_{2Norb}), 2.59 (sept, J_{HH} = 6.8 Hz, 1H, CH_{iPr-Dip}), 2.76 (m, 1H, CH_{bridgehead}), 3.35 (overlapped, 1H, CH_{iPr-Dip}), 3.45 (m, 1H, CH_{bridgehead}), 5.87 (dd, J_{HP} = 2.3 Hz, J_{HH} = 1.2 Hz, 1H, Si-satellite: J_{HSi} = 240.5 Hz, Si-H), 7.06 (d, J_{HH} = 7.1 Hz, 1H, CH_{Ar}), 7.17 (dd, J_{HH} = 2.8 and 6.4 Hz, 1H, CH_{Ar}), 7.32 (t, J_{HH} = 7.5 Hz, 1H, CH_{Ar}), 7.4-7.42 (m, 2H, CH_{Ar}), 7.56 (td, J_{HH} = 7.6 and 1.4 Hz, 1H, CH_{Ar}), 7.59 (s, 4H, *p*-CH_{BAr}), 7.73 (d, J_{HH} = 7.5 Hz, 1H, CH_{Ar}), 7.81 (s, 8H, *m*-CH_{BAr}), 8.46 (d, J_{HP} = 23.2 Hz, 1H, C=CH). ¹³C{¹H} NMR (75 MHz, -25 °C, THF-*d*₈): δ = 4.0 (d, J_{CP} = 2.1 Hz, SiMe₂), 4.3 (d, J_{CP} = 1.4 Hz, SiMe₂), 22.4 (CH_{3iPr-Dip}), 24.0 (CH_{3iPr-Dip}), 24.3 (CH_{3iPr-Dip}), 26.4 (CH_{3iPr-Dip}), 26.4 (CH_{2Norb}), 28.4 (CH_{2Norb}), 28.8 (CH_{iPr-Dip}), 29.5 (CH_{iPr-Dip}), 32.4 (d, J_{CP} = 5.2 Hz, CH_{3tBu}), 32.8 (d, J_{CP} = 5.9 Hz, CH_{3tBu}), 43.6 (d, J_{CP} = 10.4 Hz, CH_{bridgehead}), 46.6 (d, J_{CP} = 5.9 Hz, CH_{2Norb}), 47.3 (d, J_{CP} = 10.8 Hz, CH_{bridgehead}), 54.3 (d, J_{CP} = 2.1 Hz, C_{tBu}), 54.3 (d, J_{CP} = 1.0 Hz, C_{tBu}), 98.3 (d, J_{CP} = 128.6 Hz, NC=C_P), 118.0 (br sept, J_{CF} = 4.2 Hz, *p*-CH_{BAr}), 125.4 (q, J_{CF} = 272.5 Hz, CF₃), 125.8 (CH_{Ar-Dip}), 125.9 (CH_{Ar-Dip}), 126.8 (Si-C_{Ar}), 129.6 (CH_{Ar-Ph}), 129.8 (qq, J_{CF} = 31.5 Hz, J_{CB} = 2.7 Hz, *m*-C_{BAr}), 130.1 (CH_{Ar-Dip}),

132.2 ($\text{CH}_{\text{Ar-Ph}}$), 132.7 (d, $J_{\text{CP}} = 3.8$ Hz, $\text{C}=\text{C}-\text{C}_{\text{Ar}}$), 133.7 (d, $J_{\text{CP}} = 1.7$ Hz, $\text{CH}_{\text{Ar-Ph}}$), 134.8 (d, $J_{\text{CP}} = 0.8$ Hz, $\text{CH}_{\text{Ar-Ph}}$), 134.9 ($\text{N}-\text{C}_{\text{Ar}}$), 135.4 ($\text{o}-\text{CH}_{\text{BAr}}$), 146.6 ($\text{iPr}-\text{C}_{\text{Ar}}$), 147.8 ($\text{iPr}-\text{C}_{\text{Ar}}$), 148.9 (d, $J_{\text{CP}} = 23.6$ Hz, $\text{P}-\text{C}=\text{CH}$), 162.7 (q, $J_{\text{CB}} = 49.8$ Hz, $\text{isop}-\text{C}_{\text{BAr}}$), 166.5 (d, $J_{\text{CP}} = 2.8$ Hz, $\text{P}-\text{C}=\text{CH}$), 182.0 (d, $J_{\text{CP}} = 9.4$ Hz, $\text{NC}=\text{CP}$). $^{31}\text{P}\{\text{H}\}$ NMR (121 MHz, 25 °C, THF- d_8): $\delta = 23.3$ (Si-P). $^{29}\text{Si}\{\text{H}\}$ NMR (59 MHz, 25 °C, THF- d_8): $\delta = 18.9$ (d, $J_{\text{CP}} = 1.8$ Hz, SiMe_2), -8.3 (d, $J_{\text{SiP}} = 20.0$ Hz, N-Si-P). $^{11}\text{B}\{\text{H}\}$ (96 MHz, 25 °C, THF- d_8): $\delta = -6.5$ (BAr). $^{19}\text{F}\{\text{H}\}$ (282 MHz, 25 °C, THF- d_8): $\delta = -63.3$ (CF_3).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://>.

Detailed experimental procedures and spectroscopic data for all new compounds, and DFT calculation details (PDF).

Accession Codes

CCDC 2238364–2238369, 2240725 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

Any additional relevant notes should be placed here.

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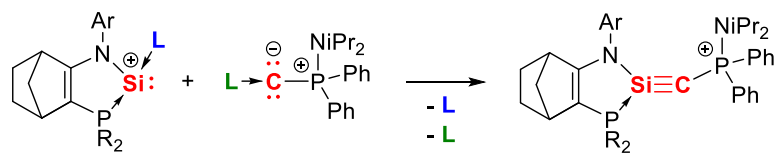
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Persistent at RT ($t_{1/2}$ = 7 days)
 Unique and rich reactivity as **silyne**

A base-stabilized C-phosphonio-*Si*-amino-silyne was successfully synthesized through a coupling reaction between two Lewis-base-stabilized low-valent species: a silyliumylidene ion and a P,S-bis-ylide. This new cationic silyne exhibits an enhanced stability ($t_{1/2}$ = 7 days at RT) and a high and rich reactivity, thanks to the dual reactivity of phosphonio substituent.