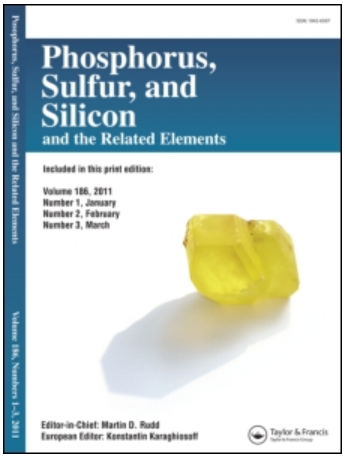

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Synthesis and Characterization of Mixed-Substituent P- n -Propyl-N-trimethylsilylphosphoranimines

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SYNTHESIS AND CHARACTERIZATION OF MIXED-SUBSTITUENT P-*n*-PROPYL-N-TRIMETHYLSILYLPHOSPHORANIMINES

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One approach to the synthesis of polyphosphazenes is the condensation polymerization of phosphoranimines. In this work, several novel P-n-propyl-N-trimethylsilylphosphoranimines have been synthesized and characterized. Modifications to the literature synthetic routes were required to obtain the precursor phosphines. The N-trimethylsilylphosphoranimines were obtained though oxidation of the phosphine with bromine and then subsequent nucleophilic displacement using lithium phenoxide. These phosphoranimines were stable for long periods of time under dry inert conditions. NMR analyses revealed complex splitting patterns beyond typical coupling due to the stereocenter at phosphorus. We report several approaches to the n-propyl containing phosphines and phosphoranimines.

Keywords: Characterization; phosphines; phosphoranimines; stereocenter; synthesis

Polyphosphazenes can have a wide variety of properties depending on the substituents on the P-N backbone, and this versatility gives polyphosphazenes potential advantages over other polymer systems for a variety of applications.[1–4] Two general methods are employed for polyphosphazene synthesis: ring opening polymerization (ROP) and condensation polymerization.

The most recognized process for polyphosphazene synthesis is the ROP route developed by Allcock and coworkers.[5] The cyclic trimer,

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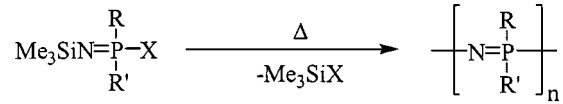
hexachlorocyclotriphosphazene, is thermally ring opened to produce hydrolytically unstable poly(dichlorophosphazene). Stable polymers are generated through nucleophilic displacement of chlorine, mainly with amines, aryloxides, and alkoxides. This synthetic order is immutable as a fully substituted cyclic phosphazene will not polymerize, hence substitution at phosphorus must be carried out after polymerization. To form polyphosphazenes via the ROP route with direct P-C linkages requires reactions using organometallic reagents, such as Grignards, but these reactions give only partial substitution at the phosphorus center.[6] Even under forcing conditions, the alkyl or aryl substitutions are incomplete, and in some cases polymer degradation or undesired side reactions occur. Therefore, alkyl and aryl substitution must be accomplished by a different technique.

The other well-known process for polyphosphazene synthesis is the condensation polymerization developed by Neilson and Wisian-Neilson (Scheme 1).[7–10] The condensation polymerization method provides a useful alternative route to stable alkyl and aryl polyphosphazenes where the functional groups are incorporated prior to polymerization. A further advantage of the condensation route is that mixed substituent homopolymers can be synthesized readily. Whereas, nucleophilic substitution of the ROP derived polydichlorophosphazene with two substituents results only in the synthesis of random terpolymers.

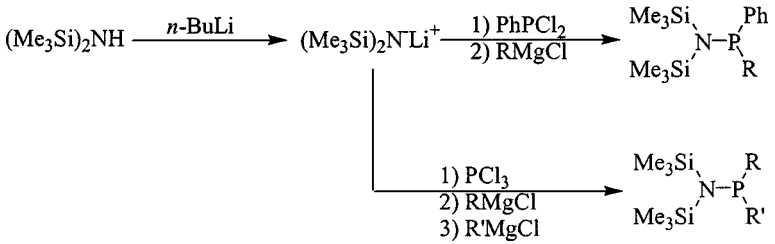


R = alkyl
R' = alkyl, phenyl
X = Cl, Br, fluoroalkoxy, phenoxy

SCHEME 1

A wide variety of alkyl and aryl N,N-bis(trimethylsilyl)aminophosphines, $(Me_3Si)_2NP(R)(R')$, have been prepared using the Wilburn method (Scheme 2).[11–17] The first step in producing phosphazenes via the condensation route is the synthesis of $(Me_3Si)_2NP(R)(R')$ which generally proceeds through a one-pot reaction where reagents are added sequentially. Conversion of $(Me_3Si)_2NP(R)(R')$ to halo-N-trimethylsilylphosphoranimines, $(Me_3Si)N{=}P(R)(R')(Br)$, is accomplished by using oxidizing agents, such as Br_2.[16,17] Displacement of bromine with oxo-nucleophiles yields potential mixed substituent homopolymer precursors.[7]

Neilson and Wisian-Neilson developed a successful method for synthesizing many types of dialkyl and alkyl/aryl polyphosphazenes.[7]



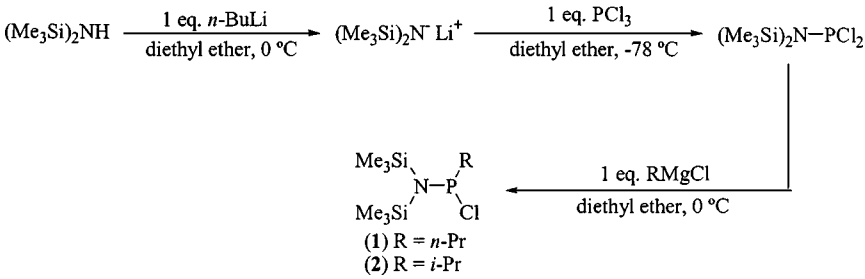
SCHEME 2

Their route yielded several symmetrical and unsymmetrical N-trimethylsilylphosphoranimines containing either methyl or phenyl groups.[11,12] Other synthetic pathways have synthesized $(Me_3Si)_2NP(R)(Cl)$, $(Me_3Si)_2NP(R)(Br)$ and the corresponding $(Me_3Si)N{=}P(R)(Br)_2$ where R is an alkyl or aryl. Previously, these products were obtained only through the attachment of sterically bulky groups, such as *t*-butyl.[19] Later, others have isolated and characterized some monoalkylated chlorophosphines,[20] yet many of these compounds were intermediates for other reactions.[11,12,14–18] In this contribution, we report the synthesis of mixed-substituent phosphoranimines containing *n*-propyl groups.

RESULTS AND DISCUSSION

P-*n*-Propyl-N,N-bis(trimethylsilyl)aminophosphines, 1–9

The Wilburn method[13] was utilized for the synthesis of **1** and **2**, $(Me_3Si)_2NP(n\text{-}Pr)(Cl)$ and $(Me_3Si)_2NP(i\text{-}Pr)(Cl)$, respectively.[18,20] The key step in these reactions is the addition of only one equivalent of Grignard in the final step of the reaction sequence (Scheme 3). The reaction yielded nearly pure **2**, however, the synthesis of **1** afforded a slight mixture of products with its analogous dialkylated



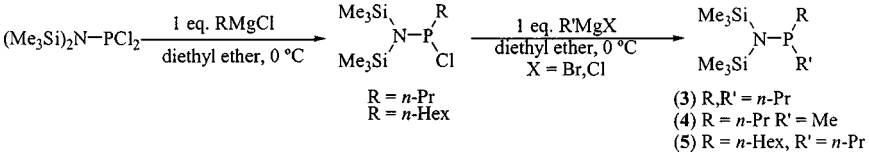
SCHEME 3

product. Integration of the resonances obtained by ^{31}P NMR spectroscopy showed an 83% conversion to **1** was achieved with the balance comprised of the dialkylated phosphine side-product. Vacuum distillation with a fractionation column failed to separate these two products.

$^{31}P\{^{1}H\}$ NMR spectroscopic analyses of **1** and **2** gave the expected phosphorus(III) downfield shifts at 160 and 164 ppm respectively. The ^{1}H NMR spectrum of **1** shows multiplets at 2.48–2.60 and 1.68–1.82 ppm, and a triplet at 1.28 ppm. The $^{13}C\{^{1}H\}$ NMR spectrum reveals C-P spin-coupling with the α (44 Hz), β (26 Hz), and γ (15 Hz) carbon nuclei.

The NMR spectral properties of **2** are significantly different from **1**. Compound **2** has diastereotopic *i*-propyl methyl groups that are clearly evident in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra (Figure 1). The *i*-propyl methyl groups are unique regardless of the rotation around the phosphorus carbon bond (Figure 2). As a result, the NMR spectra of the *i*-propyl methyl groups became more complicated with two sets of doublet of doublets in the ^{1}H NMR spectrum and two sets of doublets in the $^{13}C\{^{1}H\}$ NMR spectrum. In addition, the ^{1}H NMR spectrum of **2** with phosphorus decoupling reduces the resonance for the protons of the *i*-propyl methyl groups to two doublets.

$(Me_3Si)_2NP(n\text{-}Pr)_2$, **3**, and $(Me_3Si)_2NP(n\text{-}Pr)(Me)$, **4**, were synthesized according to reported literature procedures.[11,12] The $(Me_3Si)_2NP(n\text{-}Pr)(n\text{-}Hex)$, **5**, was obtained through addition of the larger alkyl Grignard to generate the corresponding chlorophosphine in situ, followed by the addition of the smaller alkyl Grignard (Scheme 4). Sequential addition was found to limit the amount of di-*n*-propyl phosphine through simple steric hindrance created by the larger alkyl nucleophile.



SCHEME 4

The ^{31}P NMR spectra for **3** and **4** are consistent with data reported in the literature.[11] The ^{31}P NMR resonance of **5** was slightly upfield as compared to signals for **3** and **4** (Table I). The ^{1}H NMR spectrum of **5** exhibited the resonance for the phosphorus bound *n*-propyl CH_2 group further downfield with respect to the other methylene groups.

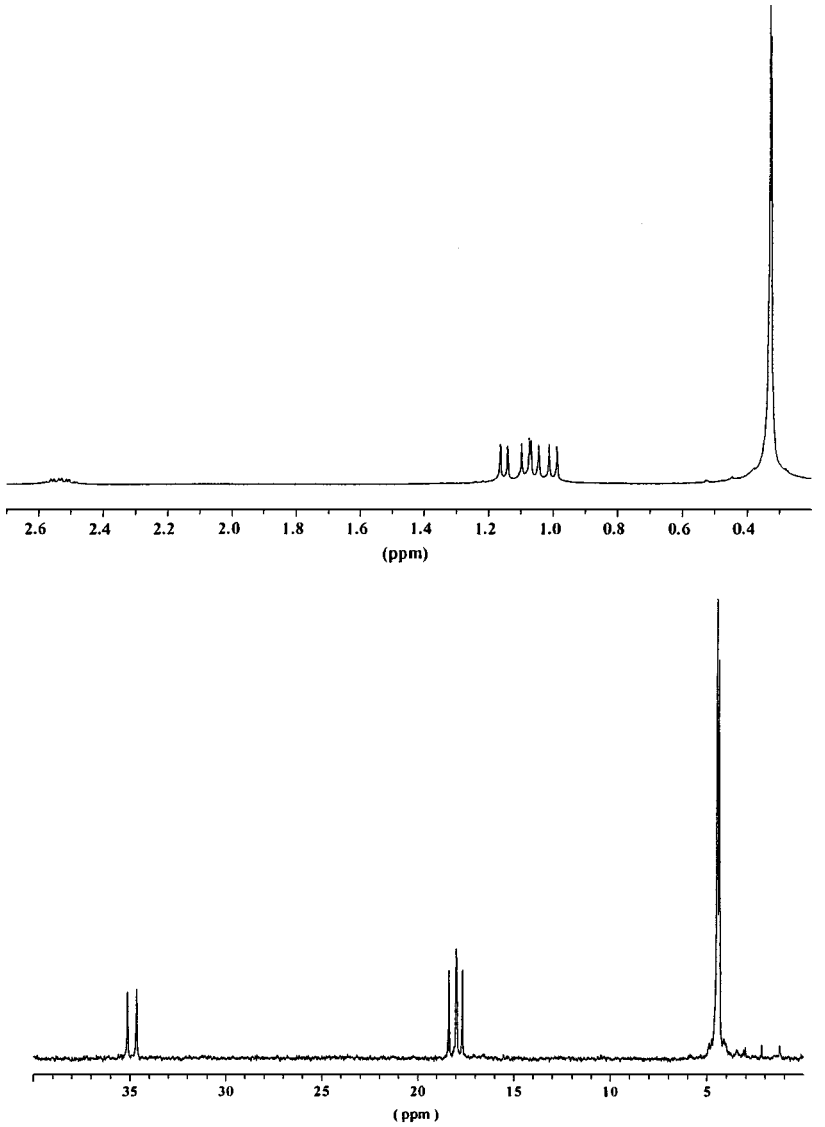


FIGURE 1 ^{1}H (upper) and $^{13}C\{^{1}H\}$ (lower) NMR spectra of $(Me_3Si)_2NP(i\text{-}Pr)(Cl)$ (**2**) ($CDCl_3$).

The terminal methyl groups of the *n*-hexyl and *n*-propyl alkyl chains are clearly evident by separate triplets.

Compound **6**, $(Me_3Si)_2NP(n\text{-}Pr)(i\text{-}Pr)$, could not be synthesized using the one-pot Wilburn method. It was found that the *n*-propyl Grignard

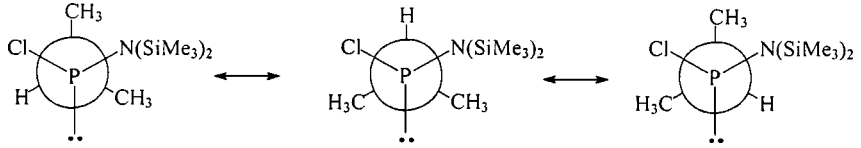
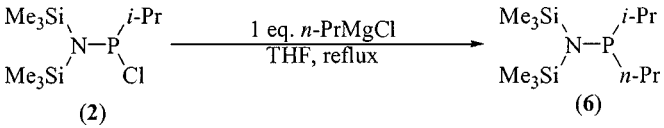


FIGURE 2 Newman Projections of $(Me_3Si)_2NP(n\text{-}Pr)(Cl)$, **2**, across the P–C bond.

did not react with $(Me_3Si)_2NP(i\text{-}Pr)(Cl)$ in diethyl ether or THF using the previous reaction conditions. Application of vigorous reflux conditions gave multiple products that were not separable through vacuum distillation. It was determined that **2** had to be isolated first to produce **6**. The rate of reaction between *n*-propyl Grignard and **2** is almost non-existent at room temperature. The temperature was elevated to a light reflux in THF, affording **6** (Scheme 5).



SCHEME 5

The ^{31}P NMR resonance for **6** (63.9 ppm) is downfield with respect to the other dialkyl phosphines possibly due to steric interactions with the two side groups. The ^{1}H NMR spectrum of **6** is similar to **2**, in which there is additional splitting of the *i*-propyl methyl protons resulting from the diastereotopic nature of their environment. Further complicating this region of the spectrum are the *n*-propyl methyl protons that gave a coincidental triplet with the diastereotopic doublet of doublets (Figure 3). The $^{13}C\{^{1}H\}$ NMR spectrum of **6** also exhibits resonances that are consistent with the diastereotopic methyls on the *i*-propyl group. In addition, the signals for the *n*-propyl group were consistent with **3**.

The nucleophilic displacement of chlorine from **1** was performed with lithium 2,2,2-trifluoroethoxide or lithium phenoxide to form **7** and **8** (Scheme 6). The chemical shift of the resonance of the ^{31}P NMR spectrum of **7** was downfield relative to its chlorophosphine analog (166 ppm) whereas **8** was slightly upfield (155 ppm). These values were consistent with the previous examples (Table I).[20] The methylene protons of the CF_3CH_2O- group in **7** displayed a pentet at 3.96 ppm in

TABLE I ^{31}P NMR of Synthesized Compounds **1–16**

No.	Phosphines	^{31}P NMR ($CDCl_3$) ppm	No.	Phosphoranimines	^{31}P NMR ($CDCl_3$) ppm
1	$(Me_3Si)_2NP(n\text{-}Pr)(Cl)$	159.8		—	
2	$(Me_3Si)_2NP(i\text{-}Pr)(Cl)$	164.2		—	
3	$(Me_3Si)_2NP(n\text{-}Pr)_2$	49.6	**10**	$(Me_3Si)N{=}P(n\text{-}Pr)_2(OPh)$	35.6
4	$(Me_3Si)_2NP(n\text{-}Pr)(Me)$	50.1	**11**	$(Me_3Si)N{=}P(n\text{-}Pr)(Me)(OPh)$	36.2
5	$(Me_3Si)_2NP(n\text{-}Pr)(n\text{-}Hex)$	40.3	**12**	$(Me_3Si)N{=}P(n\text{-}Pr)(n\text{-}Hex)(OPh)$	32.0
6	$(Me_3Si)_2NP(n\text{-}Pr)(i\text{-}Pr)$	63.9	**13**	$(Me_3Si)N{=}P(n\text{-}Pr)(i\text{-}Pr)(OPh)$	37.7
7	$(Me_3Si)_2NP(n\text{-}Pr)(OCH_2CF_3)$	166.7	**14**	$(Me_3Si)N{=}P(n\text{-}Pr)(OCH_2CF_3)(OPh)$	16.1
8	$(Me_3Si)_2NP(n\text{-}Pr)(OPh)$	154.7	**15**	$(Me_3Si)N{=}P(n\text{-}Pr)(OPh)_2$	10.7
9	$(Me_3Si)_2NP(n\text{-}Pr)(Ph)$	47.8	**16**	$(Me_3Si)N{=}P(n\text{-}Pr)(Ph)(OPh)$	22.5

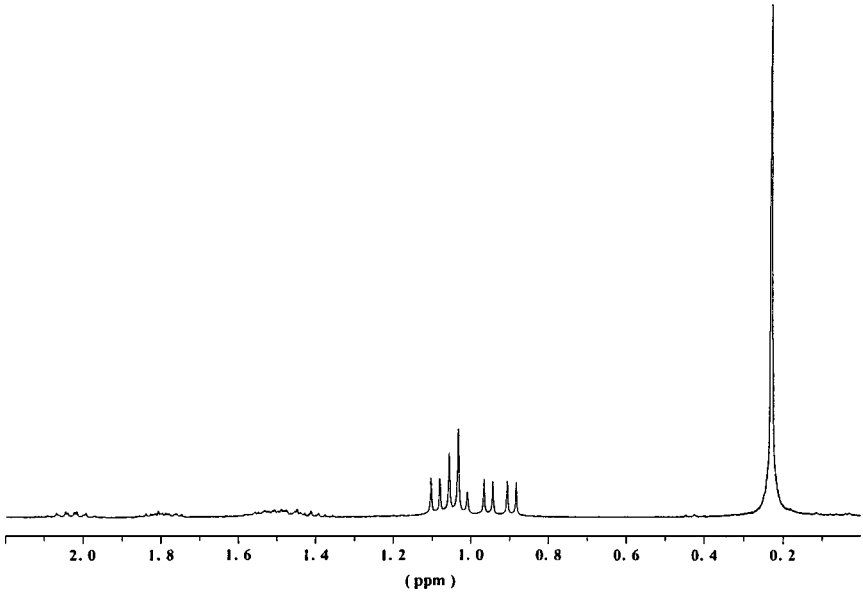
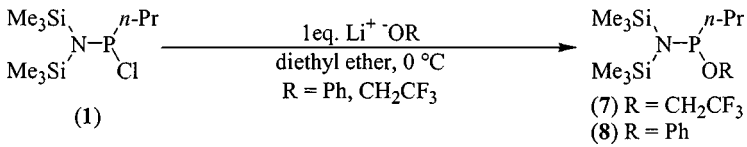


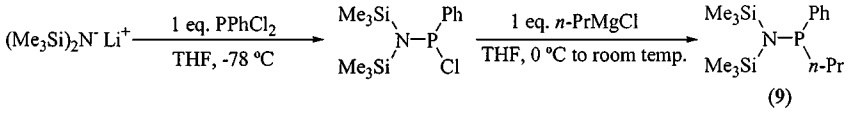
FIGURE 3 ^{1}H NMR spectrum of $(Me_3Si)_2NP(n\text{-}Pr)(i\text{-}Pr)$ (**6**) ($CDCl_3$).



SCHEME 6

the ^{1}H NMR spectrum due to the coupling with fluorine and the CH_2 group of **8**, α to the phosphorus, exhibited diastereotopic hydrogens. Phosphorus coupling was observed at the phenoxy substituent as additional splitting patterns in the aromatic region of the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **8**.

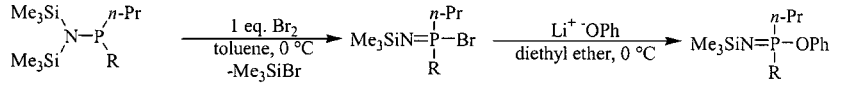
The reaction method for the formation of **9** was similar to the previous synthesis, however, phenyldichlorophosphine was used to generate $(Me_3Si)_2NP(Ph)(Cl)$ (Scheme 7). The addition of the *n*-propyl Grignard went to completion at room temperature using THF as the solvent. The ^{31}P NMR spectrum of **9** was comparable to the other bis-alkylphosphines (Table I). Additionally, the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were consistent with the proposed structure.



SCHEME 7

P-*n*-Propyl-P-phenoxy-N-trimethylsilylphosphoranimines, 10–16

Oxidation of phosphines **3** through **9** with bromine has been accomplished using the method of Neilson and Wisian-Neilson.[7] In their method, benzene was employed as the solvent, however, in this study, toluene was successfully used without difficulty. Bromine was added slowly to each phosphine at 0°C (Scheme 8). Although the bromophosphoranimine intermediates were not isolated, the phenoxide readily displaces the bromine to yield the corresponding phosphoranimines, **10–16**.



(**3**) R = *n*-Pr
(**4**) R = Me
(**5**) R = *n*-Hex
(**6**) R = *i*-Pr
(**7**) R = OCH_2CF_3
(**8**) R = OPh
(**9**) R = Ph

(**10**) R = *n*-Pr
(**11**) R = Me
(**12**) R = *n*-Hex
(**13**) R = *i*-Pr
(**14**) R = OCH_2CF_3
(**15**) R = OPh
(**16**) R = Ph

SCHEME 8

Isolation of products was performed using a flash vacuum distillation process. It was found that the salt coproducts could not be entirely separated by simple washing of the phosphoranimine with hexanes without creating an intractable residue. Even common techniques using fractional amounts of hexanes could not separate the residue. However, the product was separated from the residue by vacuum distillation, utilizing heated glassware to minimize decomposition of the product. Special precautions were taken because the products have distillation temperatures close to their decomposition temperatures, especially **11**, **15**, and **16**. Overall, these phosphoranimines were stable under dry, inert conditions for extended periods.

Most of the ^{31}P NMR spectra for the dialkyl phosphoranimines, **10–13**, exhibit similar chemical shifts, 32–38 ppm, while **16** was slightly upfield at 23 ppm. In contrast, the 2,2,2-trifluoroethoxy, **14**, and the phenoxy, **15**, clearly showed an upfield shift (16 and 10 ppm respectively) in

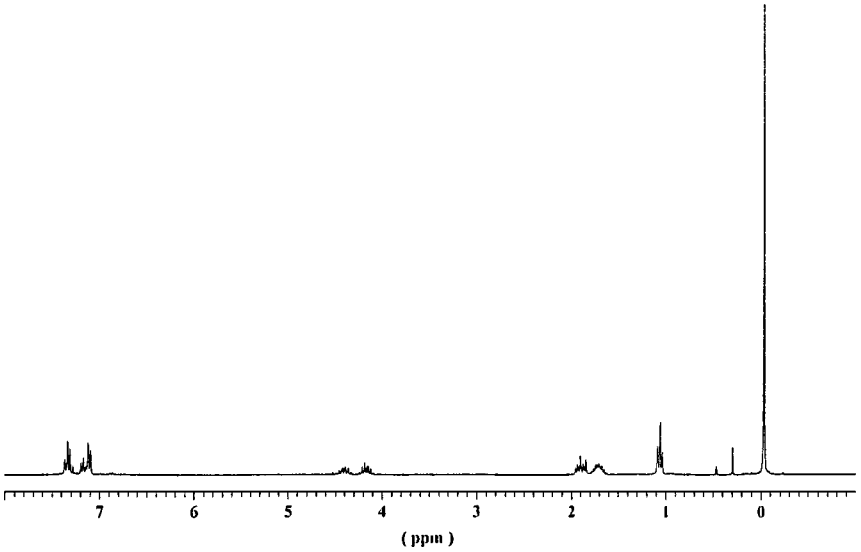


FIGURE 4 ^{1}H NMR spectrum of $(Me_3Si)N{=}P(n\text{-}Pr)(OCH_2CF_3)(OPh)$ (**14**) ($CDCl_3$).

the ^{31}P NMR spectra due to the attachment through oxygen rather than a carbon linkage. The ^{1}H NMR spectra for compounds **10–16** were more difficult to categorize. The chemical shifts and coupling constants were fairly consistent for the phenoxy group on all of the isolated phosphoranimines. However, the ^{1}H NMR spectrum of **14** showed diastereotopic hydrogens on the methylene group on CF_3CH_2O- (Figure 4) and **13** displayed diastereotopic methyl groups as seen before with its analogous phosphine, **6**. The ^{13}C NMR spectra of **10–16** did not show the same trend in coupling constants as for the phosphines **1–9**. The J^1_{CP} for the alkyl chains were determined to be 90–145 Hz, 2–8 Hz for J^2_{CP}, and 20–25 Hz for J^3_{CP}, consistent with a trend found with other alkylphosphorus(V) compounds.[11]

CONCLUSIONS

A facile route to new mixed-substituent phosphines has been devised where few undesirable side products are produced. Initially attached substituents that are sterically demanding, such as *i*-propyl or phenyl, appear to inhibit further substitution with larger alkyl Grignard reagents in diethyl ether. Overall, many of the previous reported synthetic pathways were modified to provide better

routes for a diverse array of mixed-substitutent phosphines and phosphoranimines.

Several of the NMR spectra for the phosphines and phosphoranimines revealed diastereotopic carbons that complicate the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra because of the phosphorus stereocenter. Several trends in the ^{31}P NMR spectra are apparent. Inductive electron withdrawing effects were clearly seen with the 2,2,2-trifluoroethoxy and the phenoxy groups giving a downfield shift with respect to the alkyl substituents (Table I). However, in the phosphoranimines, these substituents clearly showed an upfield shift in the ^{31}P NMR spectra. Another trend observed in the ^{31}P NMR spectra among the alkyl-*n*-propylphosphines and the alkyl-*n*-propylphosphoranimines is a downfield shift of the ^{31}P NMR signal with increased steric bulk around the phosphorus.

EXPERIMENTAL

Materials and General Procedures

The following reagents were obtained from Aldrich and used without further purification: $(Me_3Si)_2NH$, PCl_3, $PhPCl_2$, methyl MgBr (3.0 M in ether), *n*-propyl MgCl (2.0 M in ether), *i*-propyl MgCl (2.0 M in ether), *n*-hexyl MgCl (2.0 M in ether), *n*-butyl lithium (2.5 M in hexanes), CF_3CH_2OH, and phenol. Solvents employed were anhydrous diethyl ether, anhydrous tetrahydrofuran (THF), anhydrous toluene, and hexanes, and they were used as received from the manufacturer. Proton, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Bruker DMX 300 WB spectrometer operating at 7.04T: 300 MHz (^{1}H), 75 MHz (^{13}C) and 121 MHz (^{31}P).

Preparation of P-n-propyl-P-chloro-N,N-bis(trimethylsilyl)aminophosphine (1) and P-i-propyl-P-chloro-N,N-bis(trimethylsilyl)-aminophosphine (2)

These materials were prepared according to literature procedures.[20] **$(Me_3Si)_2NP(n\text{-}Pr)(Cl)$ (1);** [83% yield, bp = 65–75°C at 0.5–0.6 mmHg, ^{31}P NMR δ ($CDCl_3$) = (s) 159.8, ^{1}H NMR δ ($CDCl_3$) = (m, 2H) 2.48–2.60, (m, 2H) 1.68–1.82, (t, 3H, J_{HH} = 7.3 Hz) 1.28, (s, 18H) 0.32, ^{13}C NMR δ ($CDCl_3$) = (d, CH_2, J_{PC} = 43.9 Hz) 41.5, (d, CH_2, J_{PC} = 25.7 Hz) 18.6, (d, CH_3, J_{PC} = 15.2 Hz) 15.2, (d, $Si(CH_3)_3$, J_{PC} = 8.7 Hz) 4.4]. **$(Me_3Si)_2NP(i\text{-}Pr)(Cl)$ (2);** [71% yield, bp = 63–65°C at 0.5–0.6 mmHg, ^{31}P NMR δ ($CDCl_3$) = (s) 164.2,^{1}H NMR δ ($CDCl_3$) = (H, doublet of

septets, $J_{HH} = 7.1$ Hz, $J_{PH} = 2.8$ Hz) 2.54, (diastereotopic methyls) (3H, dd, $(CH_3)_A$, $J_{HH} = 7.0$ Hz, $J_{PH} = 19.9$ Hz) 1.12, (3H, dd, $(CH_3)_B$, $J_{HH} = 7.3$ Hz, $J_{PH} = 16.9$ Hz) 1.03, (18H, s) 0.34, ^{13}C NMR δ ($CDCl_3$) = (d, CH, $J_{PC} = 36.8$ Hz) 35.5, (d, $(CH_3)_A$, $J_{PC} = 29.0$ Hz) 18.6, (d, $(CH_3)_B$, $J_{PC} = 21.4$ Hz) 18.4, (d, $Si(CH_3)_3$, $J_{PC} = 8.1$ Hz) 5.0].

Preparation of P,P-bis-n-propyl-N,N-bis(trimethylsilyl)-aminophosphine (3); P-n-propyl-P-methyl-N,N-bis(trimethylsilyl)aminophosphine (4); and P-n-propyl-P-n-hexyl-N,N-bis(trimethylsilyl)-aminophosphine (5)

These materials were prepared according to literature procedures.[11] However, the larger alkyl chain Grignard reagent (1 equivalent) is added first, followed by the smaller alkyl chain Grignard reagent (1 equivalent). **$(Me_3Si)_2NP(n\text{-}Pr)_2$(3);** [73% yield, bp = 63–70°C at 0.3–0.35 mmHg, ^{31}P NMR δ ($CDCl_3$) = (s) 49.6, ^{1}H NMR δ ($CDCl_3$) = (m, 4H) 1.78–1.88, (m, 4H) 1.34–1.55, (t, 6H, $J_{HH} = 7.0$ Hz) 1.02, (d, 18H, $J_{PH} = 1.0$ Hz) 0.22, ^{13}C NMR δ ($CDCl_3$) = (d, CH_2, $J_{PC} = 18.6$ Hz) 35.2, (d, CH_2, $J_{PC} = 19.0$ Hz) 19.6, (d, CH_3, $J_{PC} = 13.3$ Hz) 16.2, (s, $Si(CH_3)_3$) 5.0]. **$(Me_3Si)_2NP(n\text{-}Pr)(Me)$ (4);** [60% yield, bp = 58–68°C at 0.25 mmHg, ^{31}P NMR δ ($CDCl_3$) = (s) 40.3, ^{1}H NMR δ ($CDCl_3$) = (m, 2H) 1.78–1.87, (m, 2H) 1.39–1.50, (d, 3H, $J_{PH} = 5.8$ Hz) 1.31, (t, 3H, $J_{HH} = 7.0$ Hz) 1.02, (s, 18H) 0.22]. **$(Me_3Si)_2NP(n\text{-}Pr)(n\text{-}Hex)$ (5);** [60% yield, bp = 76–82°C at 0.07–0.09 mmHg, ^{31}P NMR δ ($CDCl_3$) = (s) 50.1 ppm, ^{1}H NMR δ ($CDCl_3$) = (m, 2H) 1.78–1.87, (m, 8H) 1.32–1.55, (m, 4H) 1.25–1.37, (t, 3H, $J_{HH} = 7.0$ Hz) 1.03, (t, 3H, $J_{HH} = 6.9$ Hz) 0.91, (s, 18H) 0.22, ^{13}C NMR δ ($CDCl_3$) = (d, CH_2, $J_{PC} = 18.6$ Hz) 35.8, (d, CH_2, $J_{PC} = 18.4$ Hz) 33.4, (s, CH_2) 32.5, (d, CH_2, $J_{PC} = 12.6$ Hz) 31.9, (d, CH_2, $J_{PC} = 18.2$ Hz) 26.8, (s, CH_2) 23.4, (d, CH_2, $J_{PC} = 19.0$ Hz) 20.2, (d, CH_3, $J_{PC} = 13.3$ Hz) 16.8, (s, CH_3) 14.9, (s, $Si(CH_3)_3$) 5.5].

Preparation of P-n-propyl-P-i-propyl-N,N-bis(trimethylsilyl)aminophosphine (6)

A 250 mL three-neck, round bottom flask, equipped with a gas inlet, two rubber septa, and a magnetic stir bar was purged with nitrogen. Compound **2** (13.5 g, 0.050 mmol) was introduced into the flask via syringe with 100 mL of THF. This solution was cooled to 0°C, and *n*-propyl magnesium chloride (25.0 mL, 0.050 mmol) was slowly transferred to the 250 mL flask with the aid of a syringe. The reaction mixture was placed under a light reflux with stirring, overnight. After cooling to room temperature, 75% of the ether was removed by reduced pressure leaving behind a salt slurry. The slurry was washed three times with

100 mL of distilled hexane and filtered each time. The hexane was removed at reduced pressure leaving behind an oil. Fractional distillation under vacuum gave a colorless, clear liquid. **$(Me_3Si)_2NP(n\text{-}Pr)(i\text{-}Pr)$ (6);** [50% yield, bp = 80–95°C at 0.6–0.8 mmHg, ^{31}P NMR δ ($CDCl_3$) = (s) 63.9, ^1H NMR δ ($CDCl_3$) = (H, doublet of septets, J_{HH} = 7.1 Hz, J_{PH} = 2.8 Hz) 2.03, (m, 2H) 1.78–1.87, (m, 2H) 1.25–1.50, (diastereotopic methyls) (3H, dd, $(CH_3)_A$, J_{HH} = 7.0 Hz, J_{PH} = 14.1 Hz) 1.06, (3H, dd, $(CH_3)_B$, J_{HH} = 6.9 Hz, J_{PH} = 18.0 Hz) 0.92, (t, 3H, J_{HH} = 7.0 Hz) 1.03, (s, 18H) 0.23, ^{13}C NMR δ ($CDCl_3$) = (d, CH_2, J_{PC} = 21.3 Hz) 33.4, (d, CH, J_{PC} = 15.0 Hz) 28.9, (d, $(CH_3)_A$, J_{PC} = 18.1 Hz) 20.2, (d, $(CH_3)_B$, J_{PC} = 15.8 Hz) 20.1 (d, CH_2, J_{PC} = 29.3 Hz) 18.8, (d, CH_3, J_{PC} = 12.9 Hz) 16.3, (two broaden peaks, $Si(CH_3)_3$) 3.2–6.0].

Preparation of P-n-propyl-P-2,2,2-trifluoroethoxy-N,N-bis(trimethylsilyl)aminophosphine (7) and P-n-propyl-P-phenoxy-N,N-bis(trimethylsilyl)aminophosphine (8)

These materials were prepared according to literature procedures.[20] **$(Me_3Si)_2NP(n\text{-}Pr)(OCH_2CF_3)$ (7);** [67% yield, bp = 60–70°C at 0.3–0.35 mmHg, ^{31}P NMR δ ($CDCl_3$) = (s) 166.7, ^1H NMR δ ($CDCl_3$) = (pent, 2H, J_{FH} = 8.8 Hz) 3.96, (diastereotopic hydrogens) (H, m, H_A) 1.83–1.96, (H, m, H_B) 1.55–1.68, (m, 2H) 1.37–1.54, (t, 3H, J_{HH} = 7.2 Hz) 1.03, (s, 18H) 0.22, ^{13}C NMR δ ($CDCl_3$) = (doublet of quartets, CF_3, J_{PC} = 11.4 Hz, J_{FC} = 278.4 Hz) 124.1, (doublet of quartets, CH_2, J_{PC} = 20.4 Hz, J_{FC} = 35.3 Hz) 66.0, (d, CH_2, J_{PC} = 19.5 Hz) 36.2, (d, CH_2, J_{PC} = 25.7 Hz) 18.6, (d, CH_3, J_{PC} = 14.5 Hz) 15.2, (d, $Si(CH_3)_3$, J_{PC} = 8.7 Hz) 4.0]. **$(Me_3Si)_2NP(n\text{-}Pr)(OPh)$ (8);** [50% yield, bp = 95–115°C at 0.3–0.5 mmHg, ^{31}P NMR δ ($CDCl_3$) = (s) 154.7, ^1H NMR δ ($CDCl_3$) = (t, *meta*, J_{HH} = 7.4 Hz) 7.31, (d, *ortho*, J_{HH} = 8.3 Hz) 7.10, (t, *para*, J_{HH} = 7.0 Hz) 7.05, (diastereotopic hydrogens) (H, m, H_A) 2.05–2.18, (H, m, H_B) 1.72–1.90, (m, 2H) 1.53–1.72, (t, 3H, J_{HH} = 7.2 Hz) 1.13, (s, 18H) 0.31, ^{13}C NMR δ ($CDCl_3$) = (d, *ipso*, J_{PC} = 8.5 Hz) 158.0, (s, *meta*) 130.0, (s, *para*) 122.8, (d, *ortho*, J_{PC} = 10.1 Hz) 120.2, (d, CH_2, J_{PC} = 21.1 Hz) 39.9, (d, CH_2, J_{PC} = 22.5 Hz) 18.4, (d, CH_3, J_{PC} = 14.0 Hz) 16.6, (d, $Si(CH_3)_3$, J_{PC} = 3.4 Hz) 4.1].

Preparation of P-n-propyl-P-phenyl-N,N-bis(trimethylsilyl)aminophosphine (9)

A 500 mL three-neck, round bottom flask, equipped with a gas inlet, a 125 mL addition funnel, magnetic stir bar, and a rubber septum was charged with nitrogen, $(Me_3Si)_2NH$ (20.9 mL, 0.100 mmol), and THF (100 mL). The solution was cooled to 0°C, and *n*-butyl lithium (40 mL, 0.100 mmol) was added to the addition funnel via syringe. The *n*-butyl

lithium was then slowly added to the cooled solution and the addition funnel was washed with THF (30 mL). The ice bath was removed and the mixture was allowed to warm to room temperature for 1 h. The solution was cooled to −78°C in a dry ice/acetone bath for 10 min. $PhPCl_2$ (13.5 mL, 0.100 mmol) was injected via syringe into the addition funnel and slowly added to the cooled solution. THF (30 mL) was used to rinse the addition funnel. The dry ice/acetone bath was removed and the mixture was allowed to warm to room temperature for 1.5 h. The mixture was then cooled to 0°C for 10 min. The *n*-propyl Grignard reagent (50 mL, 0.100 mmol) solution was added to the addition funnel via syringe and slowly added to the reaction mixture. After warming to room temperature and stirring overnight, 75% of the THF was removed under reduced pressure, leaving behind a slurry. The slurry was washed three times with 200 mL of distilled hexanes to precipitate the salts. The supernatant was decanted into a nitrogen purged, 1000 mL round bottom flask equipped with a magnetic stir bar. The hexanes were removed at reduced pressure, leaving an oil. Fractional distillation under vacuum gave a colorless, clear liquid. **$(Me_3Si)_2NP(n\text{-}Pr)(Ph)$ (9);** [85% yield, bp = 115–120°C at 0.2–0.3 mmHg, ^{31}P NMR δ ($CDCl_3$) = (s) 47.8, ^{1}H NMR δ ($CDCl_3$) = (d, *ortho*, J_{HH} = 6.0 Hz) 7.41, (t, *meta*, J_{HH} = 7.1 Hz) 7.34, (t, *para*, J_{HH} = 7.0 Hz) 7.22, (m, 2H) 2.05–2.18, (m, 2H) 1.72–1.90, (m, 2H) 1.53–1.72, (t, 3H, J_{HH} = 7.2 Hz) 1.13, (s, 18H) 0.31, ^{13}C NMR δ ($CDCl_3$) = (d, *ipso*, J_{PC} = 22.8 Hz) 147.7, (d, *meta*, J_{PC} = 14.9 Hz) 129.4, (d, *ortho*, J_{PC} = 2.6 Hz) 128.8, (s, *para*) 127.5, (d, CH_2, J_{PC} = 22.0 Hz) 35.2, (d, CH_2, J_{PC} = 21.8 Hz) 20.5, (d, CH_3, J_{PC} = 14.7 Hz) 16.9, (d, $Si(CH_3)_3$, J_{PC} = 6.7 Hz) 4.1].

Preparation of P-n-propyl-P-phenoxy-N-trimethylsilylphosphoranimines (10–16)

The procedure is similar to previous literature with the substitution of toluene as the solvent.[16] A 250 mL three-neck, round bottom flask, equipped with a gas inlet, 60 mL addition funnel, magnetic stir bar, and a rubber septum, was purged with nitrogen. The appropriate phosphine (0.035 mmol) was added by syringe to the flask containing 150 mL of anhydrous toluene. The flask was cooled to 0°C, and bromine (2.0 mL, 0.039 mmol) was introduced to the addition funnel by syringe and mixed with 10 mL of toluene. The bromine solution was added slowly to the cooled flask with constant stirring. The addition was stopped when a yellow color persisted in the flask. The ice bath was removed, and the solution was slowly warmed to room temperature for 1.5 h. The solvent was removed at reduced pressure leaving a red-brown viscous liquid. The viscous liquid was dissolved in 100 mL of diethyl ether with stirring. A separate 100 mL three-neck, round bottom flask, equipped

with a gas inlet, 60 mL addition funnel, magnetic stir bar, and a rubber septum was purged with nitrogen. Phenol (3.7 g, 0.038 mmol) was added to that flask along with 75 mL of diethyl ether. The flask was cooled to 0°C for 10 min, and *n*-butyl lithium (15 mL, 0.038 mmol) was added to the addition funnel via syringe and slowly added to the phenol/ether solution. The solution was allowed to warm to room temperature for about one hour. The brominated phosphoranimine solution was cooled to 0°C for 10 min, and the lithium phenoxide solution was transferred to the phosphoranimine solution by cannula, directed by nitrogen flow. The solution was warmed to room temperature overnight. Reduced pressure was used to remove 75% of the ether leaving behind a salt slurry. The salt slurry was "flash" distilled under vacuum yielding a colorless, clear liquid. **$(Me_3Si)N{=}P(n\text{-}Pr)_2(OPh)$ (10);** [50% yield, bp = 90°C at 0.2 mmHg, ^{31}P NMR δ ($CDCl_3$) = (s) 35.6, ^{1}H NMR δ ($CDCl_3$) = (t, *meta*, J_{HH} = 8.0 Hz) 7.31, (d, *ortho*, J_{HH} = 7.7 Hz) 7.15, (t, *para*, J_{HH} = 6.6 Hz) 7.14, (m, 4H) 1.70–1.85, (m, 4H) 1.55–1.70, (t, 6H, J_{HH} = 7.0 Hz) 1.04, (s, 9H) −0.05]. **$(Me_3Si)N{=}P(n\text{-}Pr)(Me)(OPh)$ (11);** [53% yield, bp = 85–95°C at 0.1–0.3 mmHg, ^{31}P NMR δ ($CDCl_3$) = (s) 32.0, ^{1}H NMR δ ($CDCl_3$) = (t, *meta*, J_{HH} = 8.0 Hz) 7.22, (d, *ortho*, J_{HH} = 7.7 Hz) 6.88, (t, *para*, J_{HH} = 6.6 Hz) 6.85, (m, 4H) 1.55–1.85, (d, 2H, J_{PH} = 11.6 Hz) 1.51, (m, 3H) 0.93–1.12, (s, 18H) 0.28]. **$(Me_3Si)N{=}P(n\text{-}Pr)(n\text{-}Hex)(OPh)$ (12);** [42% yield, bp = 140–150°C at 0.25 mmHg, ^{31}P NMR δ ($CDCl_3$) = (s) 36.2, ^{1}H NMR δ ($CDCl_3$) = (t, *meta*, J_{HH} = 8.0 Hz) 7.31, (d, *ortho*, J_{HH} = 7.7 Hz) 7.15, (t, *para*, J_{HH} = 6.6 Hz) 7.14, (m, 4H) 1.69–1.87, (m, 4H) 1.50–1.69, (m, 6H) 1.25–1.50, (t, 3H, J_{HH} = 7.3 Hz) 1.04, (t, 3H, J_{HH} = 6.5 Hz) 0.91, (s, 9H) −0.06, ^{13}C NMR δ ($CDCl_3$) = (d, *ipso*, J_{PC} = 9.1 Hz) 152.5, (s, *meta*) 130.0, (s, *para*) 124.6, (d, *ortho*, J_{PC} = 4.2 Hz) 122.2, (d, CH_2, J_{PC} = 90.5 Hz) 33.4, (s, CH_2) 32.2, (d, CH_2, J_{PC} = 16.1 Hz) 31.4, (d, CH_2, J_{PC} = 90.4 Hz) 31.3, (d, CH_2, J_{PC} = 3.2 Hz) 23.6, (s, CH_2) 23.3, (d, CH_2, J_{PC} = 3.1 Hz) 17.3, (d, CH_3, J_{PC} = 17.3 Hz) 16.4, (s, CH_3) 14.9, (d, $Si(CH_3)_3$, J_{PC} = 3.3 Hz) 4.3]. **$(Me_3Si)N{=}P(n\text{-}Pr)(i\text{-}Pr)(OPh)$ (13);** [53% yield, bp = 95–105°C at 0.2–0.3 mmHg, ^{31}P NMR δ ($CDCl_3$) = (s) 37.7, ^{1}H NMR δ ($CDCl_3$) = (t, *meta*, J_{HH} = 8.3 Hz) 7.31, (d, *ortho*, J_{HH} = 8.6 Hz) 7.18, (t, *para*, J_{HH} = 7.0 Hz) 7.11, (H, septet, J_{HH} = 7.1 Hz) 2.01, (m, 2H) 1.70–1.84, (m, 2H) 1.57–1.73, (diastereotopic methyls) (3H, dd, $(CH_3)_A$, J_{HH} = 7.1 Hz, J_{PH} = 17.1 Hz) 1.25, (3H, dd, $(CH_3)_B$, J_{HH} = 7.1 Hz, J_{PH} = 18.0 Hz) 1.23, (t, 3H, J_{HH} = 7.2 Hz) 1.03, (s, 9H) −0.05, ^{13}C NMR δ ($CDCl_3$) = (d, *ipso*, J_{PC} = 9.6 Hz) 153.0, (s, *meta*) 130.0, (s, *para*) 124.4, (d, *ortho*, J_{PC} = 4.3 Hz) 122.2, (d, CH_2, J_{PC} = 86.6 Hz) 31.3, (d, CH, J_{PC} = 95.0 Hz) 30.1, (d, $(CH_3)_A$, J_{PC} = 4.0 Hz) 17.2, (d, CH_2, J_{PC} = 1.2 Hz) 17.1, (d, $(CH_3)_B$, J_{PC} = 3.3 Hz) 16.9 (d, CH_3, J_{PC} = 16.7 Hz) 16.6, (d, $Si(CH_3)_3$, J_{PC} = 2.8 Hz) 4.4]. **$(Me_3Si)N{=}P(n\text{-}Pr)(OCH_2CF_3)$ (OPh) (14);** [67% yield,

bp = 70°C at 0.15 mmHg, ^{31}P NMR δ ($CDCl_3$) = (s) 16.1, ^{1}H NMR δ ($CDCl_3$) = (t, *meta*, J_{HH} = 7.4 Hz) 7.34, (t, *para*, J_{HH} = 7.0 Hz) 7.17, (d, *ortho*, J_{HH} = 8.3 Hz) 7.11, (diastereotopic hydrogens) (H, m, H_A) 4.33–4.51, (H, 0 m, H_B) 4.09–4.25, (m, 2H) 1.84–1.95, (m, 2H) 1.62–1.80, (t, 3H, J_{HH} = 7.3 Hz) 1.06, (s, 9H) −0.03, ^{13}C NMR δ ($CDCl_3$) = (d, *ipso*, J_{PC} = 9.7 Hz) 151.6, (s, *meta*) 130.2, (s, *para*) 125.4, (d, *ortho*, J_{PC} = 4.5 Hz) 121.9, (doublet of quartets, CF_3, J_{PC} = 11.4 Hz, J_{FC} = 99.5 Hz) 121.6, (doublet of quartets, CH_2, J_{PC} = 5.8 Hz, J_{FC} = 36.9 Hz) 61.5, (d, CH_2, J_{PC} = 141.5 Hz) 31.2, (d, CH_2, J_{PC} = 5.4 Hz) 16.6, (d, CH_3, J_{PC} = 19.3 Hz) 15.4, (s, $Si(CH_3)_3$) 3.2]. **(Me_3Si)N=P(*n*-Pr)($OPh)_2$(15);** [67% yield, bp = 130–140°C at 0.25–0.3 mmHg, ^{31}P NMR δ ($CDCl_3$) = (s) 10.7, ^{1}H NMR δ ($CDCl_3$) = (t, *meta*, J_{HH} = 7.4 Hz) 7.34, (d, *ortho*, J_{HH} = 8.3 Hz) 7.17, (t, *para*, J_{HH} = 7.0 Hz) 7.15, (m, 2H) 1.90–2.07, (m, 2H) 1.70–1.87, (t, 3H, J_{HH} = 7.2 Hz) 1.09, (s, 9H) −0.19 ppm, ^{13}C NMR δ ($CDCl_3$) = (d, *ipso*, J_{PC} = 9.2 Hz) 152.1, (s, *meta*) 130.2, (s, *para*) 125.2, (d, *ortho*, J_{PC} = 4.5 Hz) 122.1, (d, CH_2, J_{PC} = 144.6 Hz) 31.9, (d, CH_2, J_{PC} = 5.2 Hz) 17.5, (d, CH_3, J_{PC} = 19.3 Hz) 16.1, (d, $Si(CH_3)_3$, J_{PC} = 3.3 Hz) 3.6]. **(Me_3Si)N=P(*n*-Pr)(Ph)(OPh) (16);** [37% yield, bp = 140–150°C at 0.25 mmHg, ^{31}P NMR δ ($CDCl_3$) = (s) 22.5, ^{1}H NMR δ ($CDCl_3$) = (m, 2H) 7.51–7.90, (m, 3H) 7.51–7.90, (t, *meta*, J_{HH} = 8.1 Hz) 7.28, (d, *ortho*, J_{HH} = 7.3 Hz) 7.09, (t, *para*, J_{HH} = 7.3 Hz) 7.08, (m, 2H) 1.97–2.10, (m, 2H) 1.40–1.75, (t, 3H, J_{HH} = 7.3 Hz) 0.99, (s, 9H) 0.00, ^{13}C NMR δ ($CDCl_3$) = (d, *ipso*, J_{PC} = 9.0 Hz) 151.9, (d, *ipso*, J_{PC} = 183.1 Hz) 133.4, (d, *meta*, J_{PC} = 10.2 Hz) 131.9, (s, *meta*) 129.4, (d, *ortho*, J_{PC} = 2.6 Hz) 128.4, (s, *para*) 123.9, (s, *ortho*) 121.3, (d, CH_2, J_{PC} = 98.9 Hz) 35.6, (d, CH_2, J_{PC} = 2.7 Hz) 16.4, (d, CH_3, J_{PC} = 18.2 Hz) 15.6, (d, $Si(CH_3)_3$, J_{PC} = 3.4 Hz) 3.6].

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