

Up-Scale Synthesis of p -(CH₂=CH)C₆H₄CH₂CH₂CH₂Cl and p -ClC₆H₄SiR₃ by CuCN-Catalyzed Coupling Reactions of Grignard Reagents with Organic Halides

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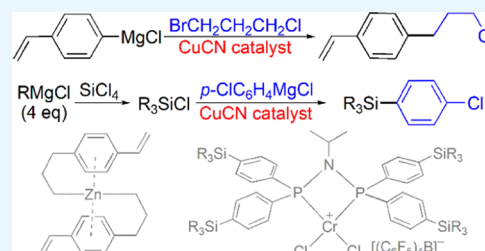
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ABSTRACT: Grignard reagents featuring carbanion characteristics are mostly unreactive toward alkyl halides and require a catalyst for the coupling reaction. With the need to prepare p -(CH₂=CH)C₆H₄CH₂CH₂CH₂Cl on a large scale, the coupling reaction of p -(CH₂=CH)C₆H₄MgCl with BrCH₂CH₂CH₂Cl was attempted to screen the catalysts, and CuCN was determined to be the best catalyst affording the desired compound in 80% yield with no formation of Wurtz coupling side product CH₂=CHC₆H₄-C₆H₄CH=CH₂. The p -(CH₂=CH)-C₆H₄Cu(CN)MgCl species was proposed as an intermediate based on the X-ray structure of PhCu(CN)Mg(THF)₄Cl. p -ClC₆H₄MgCl did not react with sterically encumbered R₃SiCl (R = *n*-Bu or *n*-octyl). However, the reaction took place with the addition of 3 mol % CuCN catalyst, affording the desired compound p -ClC₆H₄SiR₃. The structures of p -(CH₂=CH)C₆H₄CH₂CH₂CH₂MgCl and p -ClC₆H₄MgCl were also elucidated, which existed as an aggregate with MgCl₂, suggesting that some portion of the Grignard reagents were possibly lost in the coupling reaction due to coprecipitation with the byproduct MgCl₂. R₃SiCl (R = *n*-Bu or *n*-octyl) was also prepared easily and economically with no formation of R₄Si when SiCl₄ was reacted with 4 equiv of RMgCl. Using the developed syntheses, [p -(CH₂=CH)C₆H₄CH₂CH₂CH₂]₂Zn and iPrN[P(C₆H₄-*p*-SiR₃)₂]₂, which are potentially useful compounds for the production of PS-*block*-PO-*block*-PS and 1-octene, respectively, were efficiently synthesized with substantial cost reductions.



1. INTRODUCTION

Grignard reagents (RMgX, X = Cl, Br, or I) are versatile organometallic compounds, featuring carbanion (R⁻) characteristics and reacting with various types of electrophiles.^{1–5} Carbonyl compounds are a good counterpart electrophile, and nucleophilic addition reactions of Grignard reagents to carbonyl compounds are very common, occurring with no aid of catalysts.⁶ On the other hand, Grignard reagents do not react with organic halide electrophiles, typically requiring a catalyst for the coupling reactions with them. Various transition-metal-based catalysts have been developed,^{7–12} and Cu complexes among those are the oldest and most frequently employed catalyst.^{13–17} Chlorosilane compounds are known to be good counterpart electrophiles,¹⁸ but they are also unreactive in some cases, especially when either chlorosilanes or Grignard reagents are sterically encumbered (vide infra).^{19,20}

With endeavors over the past ~10 years, our team has developed an innovative production scheme for the value-added PS-*block*-PO-*block*-PS [PS, polystyrene; PO, poly(ethylene-*co*-1-alkene)], in which dialkylzinc compounds carrying styrene moieties (**2**) are essentially needed on a large scale (~30 tons per 20 kton production of triblock copolymer) (Scheme 1a).^{21–23} Dialkylzinc compounds are

typically synthesized using Grignard reagents, that is, by reacting 2 equiv of RMgX with ZnCl₂, although the purity of the isolated product has been a persistent issue.^{21,24–28} A problem encountered in the large-scale synthesis of **2** was the synthesis of the starting material p -(CH₂=CH)-C₆H₄CH₂CH₂CH₂Cl (**1**), which was also prepared using the Grignard reagent, that is, reacting p -(CH₂=CH)-C₆H₄CH₂MgCl with p TsOCH₂CH₂Cl. The latter p -toluenesulfonate compound was susceptible to the nucleophilic substitution reaction of p -(CH₂=CH)C₆H₄CH₂MgCl even in the absence of any catalyst, affording **1** in good yield (80%),²¹ but atom economy for this reaction is low (32%) with generation of a large amount of byproduct (p TsOMgCl). Furthermore, the raw materials, p TsOCH₂CH₂Cl and p -(CH₂=CH)C₆H₄CH₂Cl, are expensive. Another synthetic route for **1** was reported: reacting p -(CH₂=CH)C₆H₄MgCl

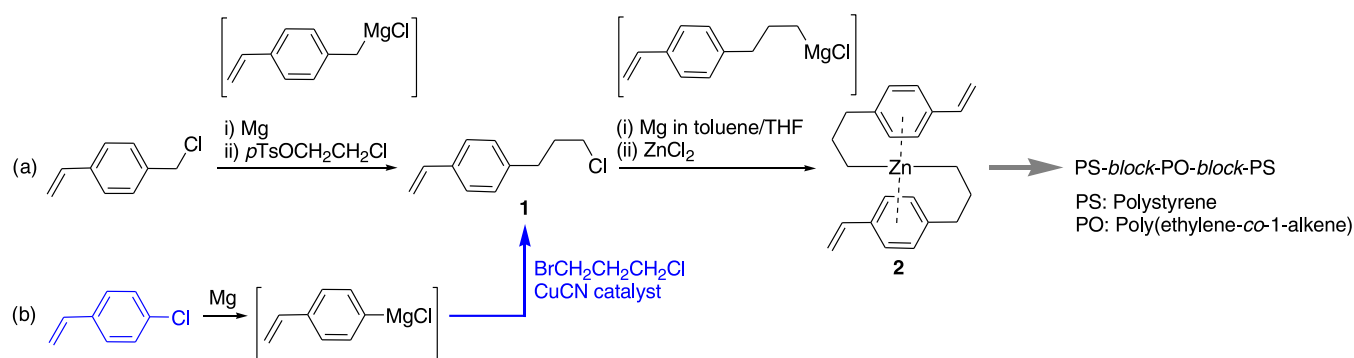
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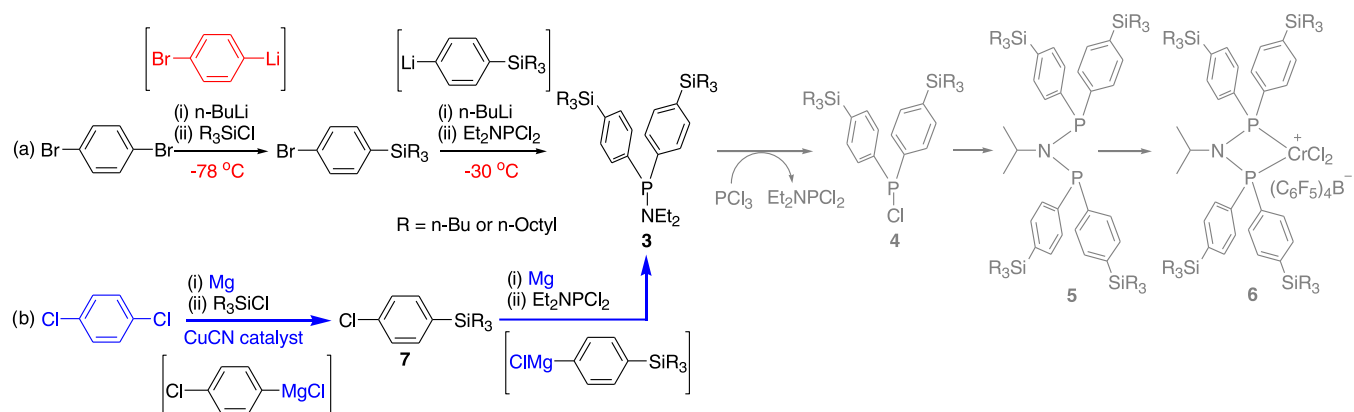
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Scheme 1. (a) Synthetic Route Previously Developed for $[p-(\text{CH}_2=\text{CH})\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2]_2\text{Zn}$ and (b) the Route Developed Herein



Scheme 2. (a) Synthetic Route Previously Developed for an Extremely Active Ethylene Tetramerization Catalyst and (b) the Route Developed Herein



with $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{Cl}$ with the aid of Li_2CuCl_4 catalyst (Scheme 1b).²⁹ The route is attractive with good atom economy (57%), benign byproduct (MgBrCl), and much lower raw material cost. However, the yield was unsatisfactorily low (49%). Therefore, we attempted to improve the yield by developing a more efficient catalyst.

In another study, our team developed an extremely active ethylene tetramerization catalyst **6** (Scheme 2), which can selectively generate 1-octene, avoiding the use of expensive methylaluminoxane (MAO) cocatalyst.^{24,30,31} For commercial operation, the catalyst should be synthesized on a large scale (~ 1 ton/100 kton products). Previously, we have demonstrated the synthesis of the target Cr catalyst **6** using organolithium compounds (Scheme 2a). However, we observed that the key intermediate $p\text{-BrC}_6\text{H}_4\text{Li}$ was explosive during its isolation process; similarly, either haloaryl-Al (e.g., $(\text{C}_6\text{F}_5)_3\text{Al}$) or haloaryl-Li (e.g., $o\text{-FC}_6\text{H}_4\text{Li}$) compounds were also reported or observed in our laboratory to be explosive.³² Moreover, the reactions performed using organolithium compounds should be operated at a low temperature of -78 or -30 °C, which may be a burden for large-scale synthesis. We attempted to replace the organolithium compounds with relatively safer Grignard reagents (Scheme 2b). However, $p\text{-ClC}_6\text{H}_4\text{MgCl}$ did not react with sterically encumbered R_3SiCl ($\text{R} = n\text{-Bu}$ or $n\text{-octyl}$), necessitating the development of a catalyst for the coupling reaction of the Grignard reagent with such bulky R_3SiCl .

2. RESULTS AND DISCUSSION

2.1. Catalyst Screening. When $p\text{-}(\text{CH}_2=\text{CH})\text{C}_6\text{H}_4\text{MgCl}$ was reacted with $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{Cl}$ in the presence of Li_2CuCl_4 catalyst (3.0 mol %) according to the reported method and conditions in our laboratory,²⁹ **1** was obtained in a low yield (11%) with formation of substantial amount of Wurtz coupling side product $\text{CH}_2=\text{CHC}_6\text{H}_4\text{-C}_6\text{H}_4\text{CH}=\text{CH}_2$ (11%). Various Cu(I) and Cu(II) complexes (CuCl , CuBr , CuI , CuCl_2 , $\text{Cu}(\text{OTf})_2$, and Li_2CuCl_4) have been used, with no special discrimination, as a catalyst for the Grignard reagent/organic halide coupling reactions, either RCu or $[\text{R}_2\text{Cu}]^-\text{[MgX]}^+$ being recognized as a key intermediate in the catalytic cycle.¹⁴ The latter “ate” complexes with Li^+ counterion (i.e., $[\text{R}_2\text{Cu}]^-\text{Li}^+$) are known as Gilman reagents, reacting well with organic halides.³³ When the same reaction was performed replacing the Li_2CuCl_4 catalyst, which is Cu(II) complex, with Cu(I) complexes such as CuCl , CuBr , and CuI , with an anticipation that a Cu(I) species such as RCu or $[\text{R}_2\text{Cu}]^-\text{[MgX]}^+$ might be more appropriately generated, yields were substantially improved (65–74%) with substantial mitigation of Wurtz coupling side product ($\sim 2\%$) (Table 1). Simple Cu(II) complexes CuCl_2 and CuBr_2 also yielded the product in much higher yields than Li_2CuCl_4 (63 and 53%); however, with formation of substantial amount of Wurtz coupling side product (6 and 12%).

CuCN has seldom been utilized as a catalyst in coupling reactions,^{34–36} although $\text{RCu}(\text{CN})\text{Li}$ species (formed by the reaction of RLi with CuCN) have been advantageously utilized in stoichiometric reactions with organic halides as a substitute

Table 1. Catalyst Screening for the Reaction of p -(CH₂=CH)C₆H₄MgCl with BrCH₂CH₂CH₂Cl (Scheme 1b)^a

catalyst	yield (%) ^b	Wurtz coupling side product (%) ^b
Li ₂ CuCl ₄	11	11
CuCl	65	1.5
CuBr	74	2.0
CuI	67	2.0
CuCl ₂	63	6.0
CuBr ₂	53	12
CuCN	80	0

^aReaction conditions: p -(CH₂=CH)C₆H₄Cl (1.00 g, 7.22 mmol), Mg (11 mmol), THF (6 mL), 5 h, then BrCH₂CH₂CH₂Cl (11 mmol), Cu complex [3.0 mol % per p -(CH₂=CH)C₆H₄Cl], 2 h at 0 °C, 10 h at 20–25 °C. ^bThe desired compound and Wurtz coupling side product could not be separated by column chromatography and yields were calculated from the combined mass and the ratios of the two compounds measured in ¹H NMR spectra (Figure S1).

for the Gilman reagent [R₂Cu]⁻Li⁺. When the coupling reaction was performed with CuCN catalyst, yield for the desired compound was the highest with negligible formation of Wurtz coupling side product, but the yield was not quantitative, limited to 80% level in any attempts, which might be attributed to coprecipitation of some portion of Grignard reagent with the generated byproduct MgCl₂ (vide infra).

CuCN was not a versatile catalyst; it worked well in the coupling reactions of p -(CH₂=CH)C₆H₄MgCl with simple primary alkyl bromides (*n*-BuBr and 1-bromo-5-pentene) to afford the desired compounds in good yields (73 and 77%) with no formation of Wurtz coupling side product, but it worked neither with secondary alkyl bromide (2-bromobutane) nor with sterically hindered primary alkyl bromide (isobutyl bromide). A significant amount of Wurtz coupling side products was generated with low yields of the desired compounds in the reactions of p -(CH₂=CH)C₆H₄MgCl with BrCH₂CH₂CH₂F or BrCH₂CH₂Cl. In the reaction of another type of Grignard reagent, p -(CH₂=CH)C₆H₄CH₂MgCl, with BrCH₂CH₂CH₂Cl, the main product was not the desired compound p -(CH₂=CH)C₆H₄CH₂CH₂CH₂CH₂Cl but the Wurtz coupling product CH₂=CHC₆H₄CH₂-CH₂C₆H₄CH=CH₂.

To investigate any intermediates formed in the catalysis, the reaction of PhMgCl with a stoichiometric amount of CuCN was performed in THF (0.50 M concentration each), in which a large amount of white solids precipitated.³⁷ The precipitates were soluble either when THF was additionally added to the reaction pot or when the isolated solids were treated with THF. From both solutions, the same type of single crystals suitable for X-ray crystallography were deposited by cooling in a freezer (-30 °C). X-ray crystallography studies revealed the formation of the anticipated RCu(CN)MgCl-type species, that is, PhCu(CN)Mg(THF)₄Cl, although it was severely disordered especially in Mg-attached THF moieties, which is the first structurally characterized magnesium cyanocuprate complex (Figure 1).³⁸ With strong Cu–CN bonds, [PhCuCN]⁻ species are formed with concomitant formation of [MgCl]⁺, but the formed [MgCl]⁺ is not an outer-sphere ion but attached to the N atom on the formed [PhCuCN]⁻ species (Mg–N distance, 2.10(5) Å); that is, the cyanide forms a bridge between Cu and Mg atoms. The ¹³C, Cu, C≡N, Mg, and Cl atoms are linearly positioned; the ¹³C–Cu–C^{CN}, Cu–

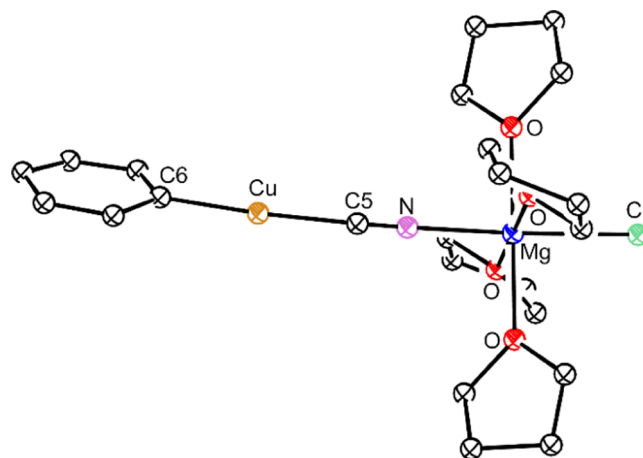


Figure 1. Thermal ellipsoid plots (30% probability level) of PhCu(CN)Mg(THF)₄Cl. Selected distances (Å) and angles (deg): Cu–C6, 1.959(17); Cu–C5, 1.97(3); C5–N, 0.99(7); N–Mg, 2.10(5); Mg–Cl, 2.512(17); C6–Cu–C5, 175.7(19); Cu–C5–N, 176(5); C5–N–Mg, 175(6); and N–Mg–Cl, 175(2).

C≡N, C≡N–Mg, and N–Mg–Cl angles were 175.7(19), 176(5), 175(6), and 175(2)°, respectively. The [MgCl]⁺ attached to [RCuCN]⁻ may facilitate the departure of bromide ion from alkyl bromide to form Mg(Br)Cl when R in [RCuCN]⁻ attacks the alkyl bromide.

2.2. Large-Scale Syntheses of 1 and 2. The Grignard reagent p -(CH₂=CH)C₆H₄MgCl was smoothly generated in a small-scale reaction [1.0 g of p -(CH₂=CH)C₆H₄Cl], even though p -(CH₂=CH)C₆H₄Cl was added in one portion to Mg powder (or turnings) dispersed in THF. However, in a large-scale reaction [10 g of p -(CH₂=CH)C₆H₄Cl in 54 g of THF], the heat generation was too vigorous to be controlled. When p -(CH₂=CH)C₆H₄Cl was added dropwise to control the temperature increase, a viscous solution was obtained, indicating polymerization of the styrene moieties. It is known fact that the Grignard reagent cannot initiate the styrene polymerization, but styrene can be polymerized in a living fashion when organic halide, Mg metal, and styrene are added in one portion (Barbier-type reaction), possibly via radical or anionic intermediate species generated at the course of Grignard reagent formation.³⁹ By changing THF solvent with a toluene/THF blend (75 g of p -(CH₂=CH)C₆H₄Cl, 450 mL of toluene, 150 g of THF), the heat generated at the course of Grignard reagent formation was controllable. p -(CH₂=CH)-C₆H₄Cl should be added in one portion to avoid the polymerization of the styrene moieties. Subsequent addition of BrCH₂CH₂CH₂Cl (1.5 equiv) and CuCN (3 mol %) to the generated p -(CH₂=CH)C₆H₄MgCl afforded desired compound 1 with no formation of the Wurtz coupling side product. In this step, occurrence of styrene moiety polymerization was also a problem: in a small-scale catalyst screening performed in THF, such side reactions of styrene moiety polymerization were negligible; however, in a large-scale synthesis performed in a toluene/THF blend solvent, such side reactions were substantial (~40%). The polymerization of the styrene moiety could be mitigated by performing the reaction in the presence of a radical scavenger at a controlled reaction temperature of 0–25 °C. Through screening the radical scavengers (4-*tert*-butylcatechol, charcoal, phenothiazine, and cupferron), cupferron ([PhN(O⁻)(N=O)] [NH₄]⁺) was determined to be the best; styrene moiety polymerization

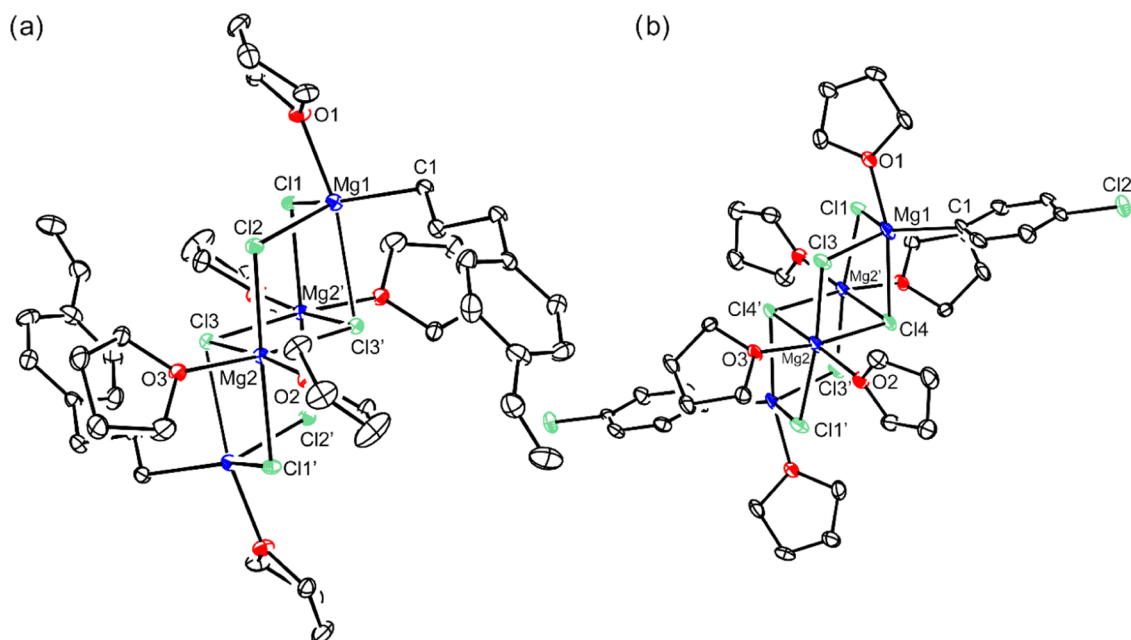


Figure 2. Thermal ellipsoid plots (30% probability level) of (a) p -($\text{CH}_2=\text{CH}$) $\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{Mg}(\text{THF})\text{Cl}-\text{Mg}(\text{THF})_2\text{Cl}_2$ and (b) p - $\text{ClC}_6\text{H}_4\text{Mg}(\text{THF})\text{Cl}-\text{Mg}(\text{THF})_2\text{Cl}_2$. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): (a) $\text{Mg1}-\text{Cl1}$, 2.1409(19); $\text{Mg1}-\text{Cl1}$, 2.3931(7); $\text{Mg1}-\text{Cl2}$, 2.4184(8); $\text{Mg1}-\text{Cl3}$, 2.8170(7); $\text{Mg1}-\text{O1}$, 2.1051(14); $\text{Mg2}-\text{Cl1}'$, 2.5104(7); $\text{Mg2}-\text{Cl2}$, 2.4709(7); $\text{Mg2}-\text{Cl3}$, 2.5098(7); $\text{Mg2}-\text{Cl3}'$, 2.5262(7); $\text{Mg2}-\text{O2}$, 2.0810(14); $\text{Mg2}-\text{O3}$, 2.0937(14); $\text{C1}-\text{Mg1}-\text{Cl1}$, 134.71(6); $\text{C1}-\text{Mg1}-\text{Cl2}$, 120.00(6); $\text{Cl1}-\text{Mg1}-\text{Cl2}$, 104.14(3); $\text{O1}-\text{Mg1}-\text{Cl3}'$, 168.82(5); $\text{Cl1}'-\text{Mg2}-\text{Cl2}$, 176.70(3); $\text{O2}-\text{Mg2}-\text{Cl3}$, 174.47(5); $\text{O3}-\text{Mg2}-\text{Cl3}$, 91.75(4); $\text{Cl3}-\text{Mg2}-\text{Cl3}'$, 85.54(2); $\text{O2}-\text{Mg2}-\text{Cl3}'$, 94.79(4); $\text{O2}-\text{Mg2}-\text{O3}$, 88.35(6); $\text{Mg1}-\text{Cl1}-\text{Mg2}'$, 99.68(2); $\text{Mg1}-\text{Cl2}-\text{Mg2}$, 101.05(2); and $\text{Mg2}-\text{Cl3}-\text{Mg2}'$, 94.46(2); (b) $\text{Mg1}-\text{Cl1}$, 2.138(10); $\text{Mg1}-\text{Cl1}$, 2.387(4); $\text{Mg1}-\text{Cl3}$, 2.391(4); $\text{Mg1}-\text{Cl4}$, 2.742(5); $\text{Mg1}-\text{O1}$, 2.099(7); $\text{Mg2}-\text{Cl1}'$, 2.473(4); $\text{Mg2}-\text{Cl3}$, 2.489(4); $\text{Mg2}-\text{Cl4}$, 2.522(4); $\text{Mg2}-\text{Cl4}'$, 2.578(4); $\text{Mg2}-\text{O2}$, 2.092(7); $\text{Mg2}-\text{O3}$, 2.062(7); $\text{C1}-\text{Mg1}-\text{Cl1}$, 123.6(3); $\text{C1}-\text{Mg1}-\text{Cl3}$, 124.5(3); $\text{Cl1}-\text{Mg1}-\text{Cl3}$, 111.73(15); $\text{O1}-\text{Mg1}-\text{Cl4}$, 166.2(3); $\text{Cl1}'-\text{Mg2}-\text{Cl3}$, 172.95(17); $\text{O2}-\text{Mg2}-\text{Cl4}'$, 169.3(3); $\text{O3}-\text{Mg2}-\text{Cl4}$, 171.9(3); $\text{O3}-\text{Mg2}-\text{Cl4}$, 95.9(2); $\text{Cl4}-\text{Mg2}-\text{Cl4}'$, 82.52(13); $\text{O2}-\text{Mg2}-\text{Cl4}$, 91.0(2); $\text{O3}-\text{Mg2}-\text{O2}$, 91.6(3); $\text{Mg1}-\text{Cl1}-\text{Mg2}'$, 100.77(15); $\text{Mg1}-\text{Cl3}-\text{Mg2}$, 98.55(15); and $\text{Mg2}-\text{Cl4}-\text{Mg2}'$, 97.48(13).

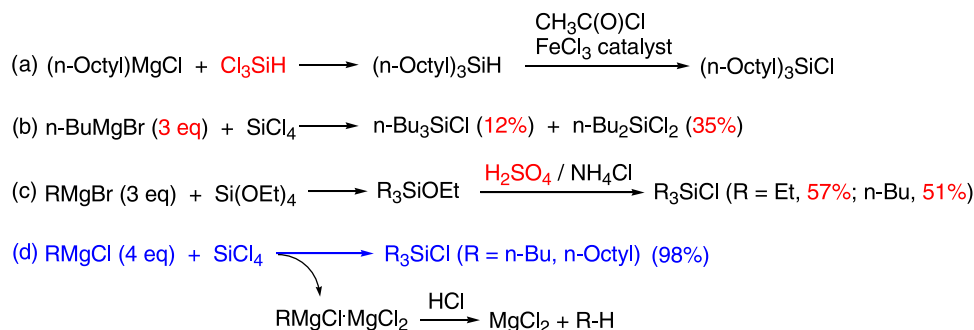
could be minimized to $\sim 8\%$ level. Quenching with acetic acid, washing with water, and distillation under full vacuum at 85°C afforded the desired product **1** in 80% yield on a 75 g scale [Figure S2 (^1H and ^{13}C NMR spectra)]

The Grignard reagent p -($\text{CH}_2=\text{CH}$)- $\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{MgCl}$ was also successfully generated from **1** under almost the same conditions and procedures employed in the synthesis of p -($\text{CH}_2=\text{CH}$) $\text{C}_6\text{H}_4\text{MgCl}$ (30 g of **1** in 160 g of toluene and 25 g of THF). Compound **1** should also be added in one portion to minimize the polymerization of styrene moieties. Heat evolution was not as severe as in the formation of p -($\text{CH}_2=\text{CH}$) $\text{C}_6\text{H}_4\text{MgCl}$, and p -($\text{CH}_2=\text{CH}$)- $\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{MgCl}$ was smoothly generated with a slight warming of the solution. Subsequent addition of ZnCl_2 to the generated p -($\text{CH}_2=\text{CH}$) $\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{MgCl}$ afforded the desired dialkylzinc compound **2** in high yield [88%, 30 g scale; Figure S3 (^1H and ^{13}C NMR spectra)]. Slightly substoichiometric amounts of ZnCl_2 [0.47 equiv per p -($\text{CH}_2=\text{CH}$)- $\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$] should be added to achieve a high yield because the addition excess ZnCl_2 detrimentally lowered the yield by the formation of RZnCl -type species. The diatomite filter aid (Celite) was reactive to R_2Zn species, whereas it was intact in the RLi or RMgX species, and the use of Celite should be avoided in the filtration process to achieve a high yield.

When the formed Grignard reagent, p -($\text{CH}_2=\text{CH}$)- $\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{MgCl}$, was stored in a freezer at -30°C , single crystals were deposited, and its structure was determined by X-ray crystallography to be a tetranuclear Mg complex formed by two p -($\text{CH}_2=\text{CH}$) $\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{Mg}(\text{THF})\text{Cl}$ -

$\text{Mg}(\text{THF})_2\text{Cl}_2$ species (Figure 2a). The same type of tetranuclear structures have also been reported for EtMgCl and $i\text{PrMgCl}$.^{40,41} Grignard reagent RMgCl in solution is under Schlenk equilibrium to form reversibly R_2Mg and MgCl_2 . The formed MgCl_2 may aggregate with RMgCl to deposit less soluble $\text{RMgCl}\cdot\text{MgCl}_2$ species. A Mg atom (Mg1) with an alkyl group can be considered to adopt a distorted trigonal bipyramidal geometry with two chlorides (Cl1 and Cl2) and C^{alkyl} (C1) forming a basal plane with Mg1 , while an O^{THF} (O1) and a chloride ($\text{Cl3}'$) occupy the axial sites (sum of bond angles of $\text{C1}-\text{Mg1}-\text{Cl1}$, $\text{C1}-\text{Mg1}-\text{Cl2}$, and $\text{Cl1}-\text{Mg1}-\text{Cl2}$, 358.9° ; $\text{O1}-\text{Mg1}-\text{Cl3}'$ bond angle, 168.8°). The other Mg atom, pertaining to MgCl_2 (Mg2), adopts a *cis*-configuration octahedral geometry coordinated by two O^{THF} atoms and four chlorides. A Mg-Cl distance is abnormally long ($\text{Mg1}-\text{Cl3}'$ distance, 2.82 Å) compared with other Mg-Cl distances around Mg1 (2.39 and 2.42 Å) and those around Mg2 (2.47–2.52 Å). Two chlorides (Cl1 and Cl2) form a μ_2 -bridge between two Mg atoms, whereas chloride (Cl3) forms a μ_3 -bridge among the three Mg atoms.

2.3. Reaction of R_3SiCl with p - $\text{ClC}_6\text{H}_4\text{MgCl}$. Grignard reagents are usually more easily generated from bromo-compounds than chloro-congeners, and p - $\text{BrC}_6\text{H}_4\text{MgBr}$ was smoothly generated from p -dibromobenzene without the aid of initiators. However, formation of some amount of side product $\text{BrMgC}_6\text{H}_4\text{MgBr}$ (ca. 5%) was inevitable in either THF or toluene/THF blend solvent. Instead, p - $\text{ClC}_6\text{H}_4\text{MgCl}$ could be generated from cheaper p -dichlorobenzene with the formation of a negligible amount of p - $\text{ClMgC}_6\text{H}_4\text{MgCl}$ (~ 1 mol %),

Scheme 3. (a–c) Synthetic Routes Previously Developed for R₃SiCl-Type Compounds and (d) the Route Developed Herein

although the I₂ initiator (0.5 mol % per Mg) and heating to 70 °C for a rather long time (18 h) were required for complete consumption of Mg in the presence of excess *p*-dichlorobenzene (1.5 equiv) in the toluene/THF blend solvent.^{42,43} Wurtz coupling side product was not detected. When R₃SiCl (R = *n*-Bu or *n*-octyl) was added to the generated *p*-ClC₆H₄MgCl, no reaction occurred, and the reactant R₃SiCl was entirely recovered through extraction with hexane. However, when CuCN (3 mol % per Mg) was added, the desired compounds, *p*-ClC₆H₄SiR₃ (7), were cleanly generated (Scheme 2b). CuCN catalysts have rarely been used in coupling reactions of Grignard reagents (or organolithium compounds) with chlorosilanes.^{44–46} Excess *p*-ClC₆H₄MgCl (~1.7 equiv Mg per R₃SiCl) was required for the complete conversion of R₃SiCl to *p*-ClC₆H₄SiR₃, which might be attributed to the loss of some portion of *p*-ClC₆H₄MgCl due to coprecipitation with MgCl₂ generated as a byproduct in the reaction, as was observed in the X-ray structures of the Grignard reagents (*vide supra*). The solids precipitated in the reaction, which might not be genuine MgCl₂ but might contain some *p*-ClC₆H₄MgCl as aggregates with MgCl₂, were rather sticky, making the filtration process tedious. Indeed, some white precipitates were observed even at the stage of (*p*-ClC₆H₄)MgCl formation, which might also be aggregates of MgCl₂, formed in the Schlenk equilibrium, with *p*-ClC₆H₄MgCl.⁴⁷ Single crystals were deposited when a solution of the formed Grignard reagent was stored in a freezer at –30 °C. X-ray crystallography studies revealed the same structure of the tetranuclear Mg complex formed by two *p*-ClC₆H₄Mg(THF)Cl·Mg(THF)₂Cl₂ species, as was observed for *p*-(CH₂=CH)C₆H₄CH₂CH₂CH₂MgCl, EtMgCl, and *i*PrMgCl (Figure 2b; *vide supra*), indicating that the Grignard reagent RMgCl seems to have a propensity to form an adduct with MgCl₂ (i.e., RMgCl·MgCl₂). When rather a high amount of I₂ (10 mol % per Mg) was added as an initiator, *p*-ClC₆H₄MgCl was completely generated in a relatively short time (12 h) without depositing the white solids, and the formed *p*-ClC₆H₄MgCl more efficiently reacted with R₃SiCl making the filtration process facile; complete conversion of R₃SiCl to *p*-ClC₆H₄SiR₃ was achieved with substantially less amount of *p*-ClC₆H₄MgCl (1.3 equiv per R₃SiCl), presumably owing to blocking the coprecipitation of *p*-ClC₆H₄MgCl with MgCl₂ with the aid of soluble MgI₂.

Using the prepared *p*-ClC₆H₄SiR₃, *p*-(R₃Si)C₆H₄MgCl was also successfully prepared using an I₂ initiator (1.5 mol %), which reacted well with Et₂NPCl₂ to afford the desired compound Et₂NP(C₆H₄-*p*-SiR₃)₂ (3 in Scheme 2b) in nearly quantitative yields. In this case, the catalyst was not required, and almost all of the generated Grignard reagent was

consumed in the reaction with Et₂NPCl₂, which, in this case, might not remain as aggregates with MgCl₂. Using the prepared compound 3, the target PNP ligands 5 (R = *n*-Bu or *n*-octyl) were prepared on a 20 g scale with >90% purity; impurities contained in 5 were *p*-(R₃Si)C₆H₄SiR₃ (3.9 wt %) and C₆H₅SiR₃ (4.9 wt %); the former was generated at the stage of *p*-ClC₆H₄SiR₃ preparation while the latter generated at the stage of *p*-(R₃Si)C₆H₄MgCl formation. Removal of these impurities was impossible; however, they were intact not only in the metalation process but also during ethylene tetramerization reactions, and Cr complex 6 prepared using the prepared PNP ligand 5 containing such impurities exhibited similar activity to that prepared using organolithium compounds according to Scheme 2a.

2.4. Preparation of R₃SiCl. In the synthetic route of PNP ligand 5, *n*-Bu₃SiCl or (*n*-octyl)₃SiCl was the only costly chemical; the others (*p*-dichlorobenzene, Mg, and PCl₃) were inexpensive, while Et₂NPCl₂ was recyclable. (*n*-octyl)₃SiCl was previously prepared from (*n*-octyl)₃SiH, which is commercially available but rather expensive, by treatment with acetyl chloride in the presence of FeCl₃ catalyst (Scheme 3a).³⁰ (*n*-octyl)₃SiH could be prepared by the reaction of (*n*-octyl)MgBr with Cl₃SiH, but the availability of Cl₃SiH has recently been restricted after some accidents with its explosiveness. *n*-Bu₃SiCl is commercially available and is expensive. Its preparation was attempted by the reaction of 3 equiv of *n*-BuMgBr with SiCl₄, but the desired product was isolated in a low yield (12%) with a main *n*-Bu₂SiCl₂ (35%) (Scheme 3b).⁴⁸ Similarly, preparation of (*n*-hexadecyl)₃SiCl was attempted by reacting 2 equiv of (*n*-hexadecyl)MgBr with (*n*-hexadecyl)SiCl₃, but the desired compound was not cleanly isolated.⁴⁹ Thus, detoured routes were developed for the synthesis of R₃SiCl type compounds. The most frequently employed method is the route via R₃SiH, as described for the synthesis of (*n*-octyl)₃SiCl in Scheme 3a.⁴⁹ Another route involves reacting RMgBr with Si(OEt)₄ to obtain R₃SiOEt, which was subsequently treated with NH₄Cl in concentrated H₂SO₄ to generate the desired *n*-Bu₃SiCl or Et₃SiCl (Scheme 3c).^{50,51}

Encouraged by the observation that R₃SiCl (R = *n*-Bu or *n*-octyl) was intact and completely recovered in the reaction with *p*-ClC₆H₄MgCl in the absence of the CuCN catalyst, we attempted to synthesize R₃SiCl directly from the reaction of SiCl₄ with RMgCl in excess, that is, 4 equiv (Scheme 3d). As previously mentioned, the reaction of SiCl₄ with 3 equiv *n*-BuMgBr was performed with the aim of preparing *n*-Bu₃SiCl, but the main product was *n*-Bu₂SiCl₂, and the desired *n*-Bu₃SiCl was obtained in low yield (Scheme 3b), which might be attributed to the loss of some portion of *n*-BuMgBr by coprecipitation with the reaction byproduct MgCl₂ (*vide*

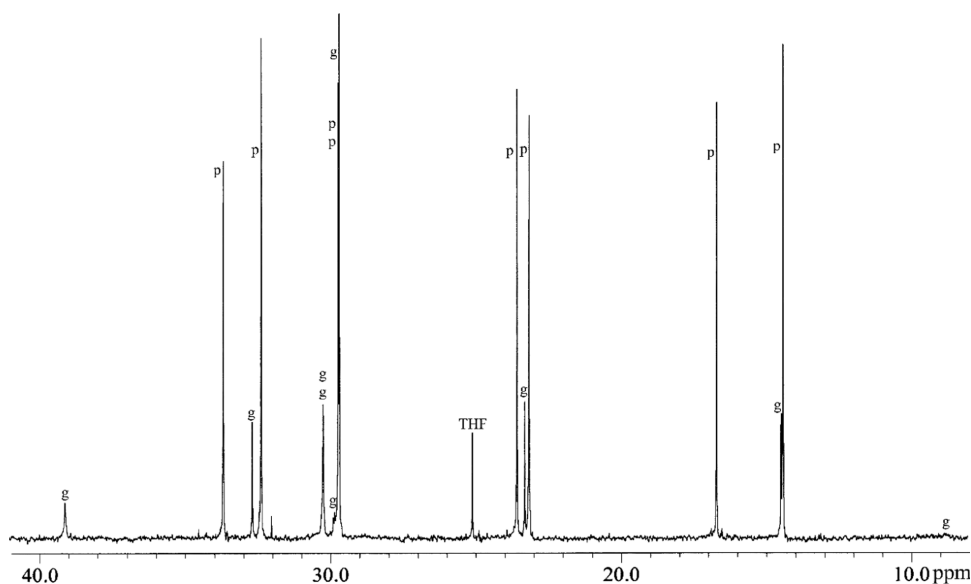


Figure 3. ^{13}C NMR spectrum of the sample taken at the final stage of the reaction of 4 equiv of (*n*-octyl) MgCl with SiCl_4 . The signals assigned to (*n*-octyl) MgCl and (*n*-octyl) $_3\text{SiCl}$ are marked with “g” and “p”, respectively.

supra). To obtain R_3SiCl , the reaction of SiCl_4 with excess RMgX (>3 equiv) has been rarely attempted because the formation of R_4Si was a concern; indeed, the synthesis of (*n*-dodecyl) $_4\text{Si}$ or (*n*-tetradecyl) $_4\text{Si}$ from the reaction of excess RMgX with SiCl_4 has been reported, although the reaction conditions were rather harsh (e.g., refluxing in xylene), and it was also reported that (*n*-octyl) $_4\text{Si}$ was readily formed in the reaction of (*n*-octyl) Li with SiCl_4 under mild condition.⁵² As expected, the desired compound (*n*-octyl) $_3\text{SiCl}$ was cleanly generated with no formation of (*n*-octyl) $_4\text{Si}$ when SiCl_4 was reacted with 4 equiv of (*n*-octyl) MgCl at a rather high temperature of 60 °C for 30 h in toluene/THF blend solvent, in which (*n*-octyl) MgCl was smoothly generated (Figure 3). The reaction was monitored by ^{13}C NMR spectroscopy (Figure S4); three sets of signals were observed after performing the reaction at 20–25 °C for 12 h. Two sets were clearly assigned to the product (*n*-octyl) $_3\text{SiCl}$ and the reactant (*n*-octyl) MgCl . The signal intensity of the rest set, which was assigned to (*n*-octyl) $_2\text{SiCl}_2$, gradually decreased with increasing reaction time and eventually disappeared after 30 h of reaction at a high temperature of 60 °C. The reaction could be also monitored by ^{29}Si NMR spectroscopy (Figure S5); two signals corresponding to (*n*-octyl) $_2\text{SiCl}_2$ and (*n*-octyl) $_3\text{SiCl}$ were observed at the middle stage of the reaction, but, eventually, one of them disappeared completely with no generation of other signals, only a signal corresponding to (*n*-octyl) $_3\text{SiCl}$ remaining.

An attempt was made to destroy (*n*-octyl) MgCl , remaining due to the excess addition, by treatment with excess Me_3SiCl ,⁵³ but it failed; most of the (*n*-octyl) MgCl remained intact with overnight stirring at 20–25 °C, possibly because it existed as aggregates with MgCl_2 (i.e., as precipitates). However, treatment with HCl (as a solution in diethyl ether) cleanly destroyed the remaining (*n*-octyl) MgCl , forming benign *n*-octane and MgCl_2 with no reaction with the formed product (*n*-octyl) $_3\text{SiCl}$. In this method, (*n*-octyl) $_3\text{SiCl}$ and *n*- Bu_3SiCl were easily, economically, and safely prepared in nearly quantitative yields. The thus-prepared (*n*-octyl) $_3\text{SiCl}$ and *n*- Bu_3SiCl could be used for the synthesis of PNP ligand **5** with a substantial cost reduction.

3. CONCLUSIONS

It was found that CuCN among the screened Cu complexes was the best catalyst for the coupling reaction of $p\text{-(CH}_2=\text{CH)C}_6\text{H}_4\text{MgCl}$ with $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{Cl}$, affording $p\text{-(CH}_2=\text{CH)C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ in high yield (80%) with no formation of Wurtz coupling side product. CuCN also effectively functioned as a catalyst for the coupling reaction of $p\text{-ClC}_6\text{H}_4\text{MgCl}$ with sterically encumbered R_3SiCl ($\text{R} = n\text{-Bu}$ or *n*-octyl), which was entirely intact in the absence of the catalyst, to afford $p\text{-ClC}_6\text{H}_4\text{SiR}_3$. The structures of $\text{PhCu}(\text{CN})\text{Mg}(\text{THF})_4\text{Cl}$, $p\text{-(CH}_2=\text{CH)C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{Mg}(\text{THF})\text{Cl}\cdot\text{Mg}(\text{THF})_2\text{Cl}_2$, and $p\text{-ClC}_6\text{H}_4\text{Mg}(\text{THF})\text{Cl}\cdot\text{Mg}(\text{THF})_2\text{Cl}_2$ were elucidated by X-ray crystallography to understand the role of the CuCN catalyst as well as why Grignard reagents are frequently required in excess in the coupling reactions. Moreover, R_3SiCl ($\text{R} = n\text{-Bu}$ or *n*-octyl) was obtained without the formation of R_4Si when 4 equiv of RMgCl was reacted with SiCl_4 . The prepared compounds were used for the large-scale synthesis of $[p\text{-(CH}_2=\text{CH)C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2]_2\text{Zn}$ and $i\text{PrN}[\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-SiR}_3)_2]_2$ with substantial cost reduction, which are potentially useful for the production of *PS-block-PO-block-PS* and 1-octene, respectively.

4. EXPERIMENTAL SECTION

4.1. Catalyst Screening. 4-Chlorostyrene (1.00 g, 7.22 mmol) was added in one portion to Mg powder (0.263 g, 10.8 mmol) dispersed in THF (6 mL). After ~1 h, the solution spontaneously warmed up, indicating that the reaction was initiated, and then the solution cooled to room temperature after maintaining the warmed state for ~0.5 h. After the reaction mixture was stirred further at 20–25 °C for ~3.5 h (total reaction time, 5 h), Mg remaining due to the excess addition was filtered off to obtain a light yellow solution. Subsequently, $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{Cl}$ (1.70 g, 10.8 mmol) and Cu complex [0.22 mmol, 3.0 mol % per $p\text{-(CH}_2=\text{CH)C}_6\text{H}_4\text{Cl}$] were successively added after the resulting solution was cooled in an ice bath. After stirring at 0 °C for 2 h and at 20–25 °C for 10 h, acetic acid (0.43 g), 4-*tert*-butylcatechol (6 mg), and

water (20 mL) were successively added. The product was extracted with toluene (3 × 7 mL), and the solvents were removed using a rotary evaporator to obtain a crude product. The crude product was purified by silica gel column chromatography and eluted with hexane. The desired product *p*-(CH₂=CH)C₆H₄CH₂CH₂CH₂Cl and the Wurtz coupling side product CH₂=CHC₆H₄-C₆H₄CH=CH₂ were not separated by column chromatography, and the ratios of the two compounds were determined by ¹H NMR analysis (Figure S1).

4.2. Large-Scale Synthesis of *p*-(CH₂=CH)-C₆H₄CH₂CH₂CH₂Cl (1). 4-Chlorostyrene (75.0 g, 541 mmol) was added in one portion to Mg powder (19.7 g, 812 mmol) dispersed in toluene (450 mL) and THF (150 g, 2.16 mol). The solution spontaneously warmed up in ~1 h, THF was spontaneously refluxed for ~0.5 h, and finally the solution cooled down to room temperature. After reaction for a total of 8 h, the excess Mg was filtered off to obtain a light yellow solution. The solution was cooled in an ice bath, and then, BrCH₂CH₂CH₂Cl (128 g, 812 mmol), cupferron (0.420 g, 27.0 mmol), and CuCN complex (1.46 g, 16.2 mmol) were successively added. After stirring at 0 °C for 2 h and then at 20–25 °C for 10 h, acetic acid (32.5 g, 541 mmol), 4-*tert*-butylcatechol (0.450 g, 27.0 mmol), and water (600 mL) were successively added. The product was extracted with toluene (3 × 200 mL), and the solvents were removed using a rotary evaporator to obtain a crude product (88.0 g). Vacuum distillation was performed at 85 °C under full evacuation to obtain the desired compound [78.8 g, 81% yield; Figure S2 (¹H and ¹³C NMR spectra)], which could be used in the next reaction without causing any problems.

4.3. Large-Scale Synthesis of [*p*-(CH₂=CH)-C₆H₄CH₂CH₂CH₂]₂Zn (2). The prepared 1 (30.0 g, 166 mmol) was added to Mg turnings (12.1 g, 498 mmol) dispersed in toluene (180 mL) and THF (24 g, 333 mmol). The solution spontaneously warmed in ~2 h and then cooled to room temperature after maintaining the warmed state for ~1 h. After reaction for 5 h, excess Mg was filtered off. ZnCl₂ (10.2 g, 78.0 mmol, 0.47 equiv per 1) was then added to the filtrate. After stirring at 20–25 °C for 12 h, the solvents were removed under vacuum. Hexane (300 g) was added and filtration was performed, with avoiding the use of a filter aid Celite, to remove the byproduct MgCl₂. The solvent was removed using a vacuum line to obtain white solids [24.5 g, yield 88%; Figure S3 (¹H and ¹³C NMR spectra)], which could be used for the synthesis of PS-*block*-PO-*block*-PS without causing any problems.

4.4. PhCu(CN)Mg(THF)₄Cl. CuCN (0.090 g, 1.0 mmol) was added to a solution of PhMgCl (1.0 mmol) in THF (1.5 mL). Gray solids precipitated upon overnight stirring at 20–25 °C, which became colorless upon heating with a heat gun with the addition of THF (~5 mL). Colorless single crystals were deposited when the solution was stored in a freezer at –30 °C for 2 days.

4.5. *p*-ClC₆H₄Si(*n*-octyl)₃. 1,4-Dichlorobenzene (7.72 g, 52.5 mmol) was added in one portion to Mg turnings (0.851 g, 35.0 mmol) dispersed in toluene (29.1 mL) and THF (10.1 g, 140 mmol), followed by I₂ (0.888 g, 3.50 mmol) addition. All Mg turnings disappeared upon stirring at 70 °C for 12 h, affording an orange-colored solution. Upon titration of the solution with I₂ in THF containing LiCl (0.50 M), yield for formation of *p*-ClC₆H₄MgCl was 88% per Mg remaining after the reaction with I₂ initiator.⁵⁴ After the resulting solution was

cooled in an ice bath, CuCN (84.6 mg, 0.945 mmol) was added, and subsequently (*n*-octyl)₃SiCl (9.53 g, 23.6 mmol) dissolved in toluene (2.91 mL) and THF (1.01 g) was added dropwise. The solution was warmed to 20–25 °C and stirred for 24 h. The solution was cooled in an ice bath, and HCl (3.70 mL, 2.13 M in diethyl ether, 7.88 mmol) was added to destroy *p*-ClC₆H₄MgCl remaining. The solution was warmed to 20–25 °C and stirred for 2 h. After all of the volatiles were removed using a vacuum line, the residue was dissolved in hexane (80 g). The insoluble fractions were removed by filtration through Celite. Removal of the solvent afforded a yellow oil, which was evacuated at 90 °C to remove unreacted 1,4-dichlorobenzene and chlorobenzene obtaining the desired compound (10.6 g, 94%). In ¹H NMR spectrum (C₆D₆), a sharp singlet signal was observed at 7.72 ppm along with the main product signals, which was tentatively assigned to disilylated side product *p*-(*n*-octyl)₃SiC₆H₄Si(*n*-octyl)₃ (1.7 wt %) (Figure S6). ¹H NMR (600 MHz, C₆D₆): δ 7.30 (d, *J* = 7.8 Hz, 2H, C₆H₄), 7.26 (d, *J* = 8.4 Hz, 2H, C₆H₄), 1.45–1.35 (12H, CH₂), 1.35–1.23 (24H, CH₂), 0.91 (t, *J* = 7.8 Hz, 9H, CH₃), 0.87–0.79 (br, 6H, SiCH₂) ppm. ¹³C{¹H} NMR (150 MHz, C₆D₆): 136.5, 135.9, 135.6, 128.4, 34.2, 32.4, 29.8, 29.7, 24.3, 23.1, 14.4, 12.8 ppm. ²⁹Si{¹H} NMR (119 MHz, C₆D₆): –1.26 ppm. HRMS(EI): *m/z* calcd. ((M⁺) C₃₀H₅₅SiCl) 478.3762, found: 478.3761. *p*-ClC₆H₄Si(*n*-Bu)₃ was prepared according to the same method and conditions using *n*-Bu₃SiCl (Figure S7). ¹H NMR (600 MHz, C₆D₆): δ 7.23 (d, *J* = 8.4 Hz, 4H, C₆H₄), 1.37–1.26 (6H, CH₂), 0.89 (t, *J* = 7.2 Hz, 9H, CH₃), 0.76–0.72 (br, 6H, SiCH₂) ppm. ¹³C{¹H} NMR (150 MHz, C₆D₆): 136.4, 135.8, 135.5, 128.4, 27.2, 26.4, 14.0, 12.4 ppm. ²⁹Si{¹H} NMR (119 MHz, C₆D₆): –1.30 ppm. HRMS(EI): *m/z* calcd. ((M⁺) C₁₈H₃₁SiCl) 310.1884, found: 310.1885.

4.6. Et₂NP(C₆H₄-*p*-SiR₃)₂ (R = *n*-octyl). *p*-ClC₆H₄Si(*n*-octyl)₃ (17.3 g, 36.1 mmol) was added in one portion to Mg purum (1.32 g, 54.2 mmol) dispersed in toluene (46 mL) and THF (16.0 g, 222 mmol) and subsequently I₂ (0.209 g, 0.823 mmol) was added. ¹H NMR analysis indicated that *p*-ClC₆H₄Si(*n*-octyl)₃ was completely converted to *p*-(*n*-octyl)₃SiC₆H₄MgCl upon stirring at 75 °C for 48 h, and the excess Mg was filtered off. The filtrate was cooled in an ice bath, and Et₂NPCL₂ (2.95 g, 17.0 mmol) dissolved in toluene (4.1 mL) and THF (1.43 g) was added dropwise. The solution was warmed to 20–25 °C and stirred for 6 h. After all of the volatiles were removed using a vacuum line, the residue was dissolved in hexane (100 g). The insoluble fraction was removed by filtration through Celite. In ¹H NMR spectrum (C₆D₆), a multiplet signal was observed at 2.82–2.74 ppm along with the main product signals, which was assigned to monoalkylated side-product Et₂NP(Cl)(C₆H₄-*p*-SiR₃) (~2.5 mol %) (Figure S8). The side product was completely removed by anchoring it to the silica surface through the formation of ≡Si–O–P(C₆H₄-*p*-SiR₃)(NEt₂) species. Thus, silica gel (2.0 g) dried overnight in an oven at 150 °C was added to the filtrate and stirred for 1 h at 20–25 °C. Filtration and removal of the solvent afforded a grayish-yellow oil (16.8 g, yield 99%), of which ¹H NMR spectrum analysis indicated that the side-product Et₂NP(Cl)(C₆H₄-*p*-SiR₃) was completely removed but the product was contaminated with another side product (*n*-octyl)₃SiC₆H₅ (3.5 wt %), which was generated at the stage of *p*-(*n*-octyl)₃SiC₆H₄MgCl formation, and *p*-(*n*-octyl)₃SiC₆H₄Si(*n*-octyl)₃ (1.5 wt %), which was formed at the stage of *p*-ClC₆H₄Si(*n*-octyl)₃ preparation (Figure S9). Et₂NP-

(C₆H₄-*p*-SiR₃)₂ (R = *n*-Bu) was also prepared according to the same method and conditions using *p*-ClC₆H₄Si(*n*-Bu)₃ (Figure S10).

4.7. (*n*-Octyl)₃SiCl. 1-Chlorooctane (13.8 g, 92.6 mmol) was added in one portion to Mg turnings (3.37 g, 139 mmol) dispersed in toluene (100 mL) and THF (13.4 g, 185 mmol) and subsequently I₂ (0.117 g, 0.463 mmol) was added. ¹H NMR analysis indicated that 1-chlorooctane was completely converted to (*n*-octyl)MgCl upon stirring at 20–25 °C for 12 h. Excess Mg was filtered off. The filtrate was cooled in an ice bath, and then SiCl₄ (3.93 g, 23.2 mmol) dissolved in toluene (4.6 mL) was added dropwise. When the resulting solution was stirred at 60 °C for 30 h, only the signals assigned to the product (*n*-octyl)₃SiCl and reactant (*n*-octyl)MgCl were observed in the ¹³C NMR spectrum (Figure 3). After cooling to room temperature, HCl (10.9 mL, 2.13 M in diethyl ether, 23.2 mmol) was added and then stirred overnight at 20–25 °C to destroy (*n*-octyl)MgCl remaining due to the excess addition. All volatiles were removed using a vacuum line and hexane (50 g) was added. The insoluble fractions were filtered off, and the solvent was removed using a vacuum line to obtain a yellow oil [9.19 g, yield 98%; Figure S11 (¹H and ¹³C NMR spectra)], which could be used in the synthesis of *p*-ClC₆H₄Si(*n*-octyl)₃ without causing any problems. (*n*-Bu)₃SiCl was prepared according to the same method and conditions using 1-chlorobutane (Figure S12).

4.8. X-Ray Crystallography. The reflection data for PhCu(CN)Mg(THF)₄Cl (CCDC #: 2203756), *p*-(CH₂=CH)C₆H₄CH₂CH₂CH₂Mg(THF)Cl·Mg(THF)₂Cl₂ (CCDC #: 2203757), and *p*-ClC₆H₄Mg(THF)Cl·Mg(THF)₂Cl₂ (CCDC #: 2203758) were collected on a Bruker APEX II CCD area diffractometer using graphite-monochromated Mo K α radiation (λ = 0.7107 Å). Specimens of suitable quality and size were selected, mounted, and centered in the X-ray beam using a video camera. The hemisphere of the reflection data was collected as φ and ω scan frames at 0.5°/frame and an exposure time of 10 s/frame. The cell parameters were determined and refined by the SMART program. Data reduction was performed using SAINT software. The data were corrected for Lorentz and polarization effects. Empirical absorption correction was applied using the SADABS program. The structures of the compounds were obtained by direct methods and refined by full-matrix least-squares methods using the SHELXTL program package and Olex2 program with anisotropic thermal parameters for all non-hydrogen atoms. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre.

4.8.1. Crystallographic Data for PhCu(CN)Mg(THF)₄Cl. C₂₃H₃₇ClCuMgNO₄, *M* = 514.83, orthorhombic, *a* = 7.8427(7), *b* = 13.4473(12), *c* = 12.7947(11) Å, *V* = 1349.4(2) Å³, *T* = 100(2) K, space group *Pnmm*, *Z* = 2, 17720 unique [*R*(int) = 0.0770] which were used in all calculations. The final *wR*₂ was 0.2194 (*I* > 2 σ (*I*)).

4.8.2. Crystallographic Data for *p*-(CH₂=CH)-C₆H₄CH₂CH₂CH₂Mg(THF)Cl·Mg(THF)₂Cl₂. C₂₃H₃₇Cl₃Mg₂O₃, *M* = 516.49, monoclinic, *a* = 10.99830(10), *b* = 18.3652(3), *c* = 13.6228(2) Å, β = 105.4132(7)°, *V* = 2652.65(6) Å³, *T* = 100(2) K, space group *P2₁/n*, *Z* = 4, 5053 unique [*R*(int) = 0.0384] which were used in all calculations. The final *wR*₂ was 0.0790 (*I* > 2 σ (*I*)).

4.8.3. Crystallographic Data for *p*-ClC₆H₄Mg(THF)Cl·Mg(THF)₂Cl₂. C₃₆H₅₆Cl₈Mg₄O₆, *M* = 965.65, triclinic, *a* = 8.7147(13), *b* = 11.4349(10), *c* = 12.7657(11) Å, α =

65.903(6), β = 83.891(8), γ = 85.851(8)°, *V* = 1154.1(2) Å³, *T* = 100(2) K, space group *P*-1, *Z* = 1, 2406 unique [*R*(int) = 0.1477] which were used in all calculations. The final *wR*₂ was 0.1697 (*I* > 2 σ (*I*)).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c05951>.

¹H NMR spectra of the crude *p*-(CH₂=CH)-C₆H₄CH₂CH₂CH₂Cl containing Wurtz coupling side product and the crude Et₂NP[C₆H₄-*p*-Si(*n*-octyl)₃]₂ containing Et₂NP(Cl)[C₆H₄-*p*-Si(*n*-octyl)₃] impurity; ¹H and ¹³C NMR spectra of *p*-(CH₂=CH)-C₆H₄CH₂CH₂CH₂Cl, [*p*-(CH₂=CH)-C₆H₄CH₂CH₂CH₂]₂Zn, *p*-ClC₆H₄SiR₃, Et₂NP(C₆H₄-*p*-SiR₃)₂, and R₃SiCl; ¹³C NMR spectra monitored for the reaction of 4 equiv (*n*-octyl)MgCl with SiCl₄; ²⁹Si NMR spectra monitored for the reaction of 4 equiv (*n*-octyl)MgCl with SiCl₄ (PDF)

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Notes

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