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**Phosphonium Salts**

# Hydrophobic Encapsulated Phosphonium Salts—Synthesis of Weakly Coordinating Cations and their Application in Wittig Reactions

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**Abstract:** Large and rigid tetraarylphosphonium tetrafluoroborate salts have been synthesized representing weakly coordinating cations with diameters of several nanometers. Divergent dendritic growth by means of thermal Diels–Alder cycloaddition was employed for the construction of the hydrophobic polyphenylene framework up to the third generation. X-ray crystal structure analysis of first-generation phosphonium tetrafluoroborate supported the rigidity of the non-collapsible shell around the phosphorus center and gave insight into solid-state packing and cation–anion distances. Copper(I)-catalyzed azide–alkyne ligation served as reliable method for the preparation of a first-generation triazolylphenyl hybrid phosphonium cation under mild reaction conditions. Furthermore, from the synthesis of triarylbenzylphosphonium bromides, Wittig precursors with unprecedented bulky substituents in the α-position were accessible. Employment of these precursors under Wittig conditions by treatment with base and subsequent reaction with aldehydes preferentially provided (*Z*)-olefins with bulky polyphenylene substituents.

## Introduction

For decades the field of weakly coordinating anions (WCAs) has been of significant interest for both academia and industry.[1] Their applications range from catalysis,[2] polymerization,[3] electrochemistry,[4] and ionic liquids[5] to battery technology.[6] Until recently the corresponding class of compounds, consequently termed weakly coordinating cations (WCCs), has hardly attracted attention. We report reliable and versatile synthetic pathways to form polyphenylene dendrimers[7] with a cationic phosphonium core. The macromolecular size is increased to control Coulombic interactions between ion pairs. We regarded phosphonium salts as suitable candidates to establish a new generation of WCCs, hydrophobic salts constituted from molecularly defined cations with diameters up to about 5 nm. In addition to synthesis we present a brief investigation of their stability against alkaline degradation in solution due to the presence of large, screening polyphenylene dendrons.

The main focus is the application of triarylbenzylphosphonium salts as Wittig reagents, bearing bulky substituents of unprecedented size in the α-position to the phosphorus. Since its introduction about 60 years ago,[8,9] the Wittig reaction has become of particular interest with regard to the stereochemistry of the initial adduct formation and the resultant (*E/Z*) olefin ratio.[10,11] A variety of factors including temperature, solvent, choice of carbonyl reagent, type of ylide as well as the presence and concentration of lithium salts were demonstrated to influence the resulting (*E/Z*) alkene ratio.[12,13] Detailed mechanistic studies by Vedejs et al.[14] investigated the role of substituents at phosphorus ylides and attributed the relevant stereochemistry to a kinetically controlled formation of *cis*- or *trans*-oxaphosphetanes. However, among the substituent effect reports so far, the moiety in the α-position of the ylide (see Scheme 5 later) was mostly limited to a simple methyl group or slightly larger alkyl homologues. Hence, we considered dendronization as a valuable tool for the introduction of an unprecedentedly large and rigid polyphenylene substituent at the phosphonium component. By employing this approach, novel alkenes with markedly large substituents became accessible.

## Results and Discussion

### Synthesis of tetraaryl-substituted polyphenylene phosphonium cations

Initially, an ethynyl-functionalized tetraphenylphosphonium derivative (**4**) was synthesized according to Scheme 1.

Grignard formation of (4-bromophenyl)trimethylsilane followed by subsequent reaction with $PCl_3$ afforded tris[4-(trimethylsilylethynyl)phenyl]phosphine (**1**). After deprotection of

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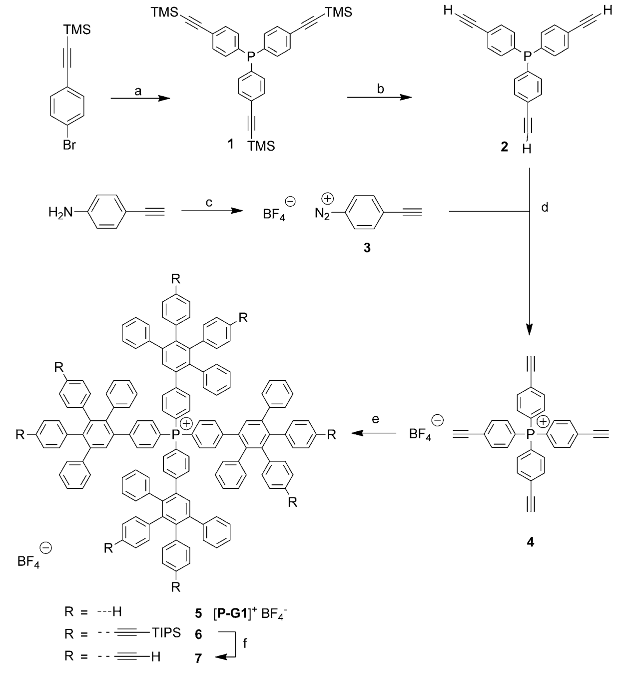
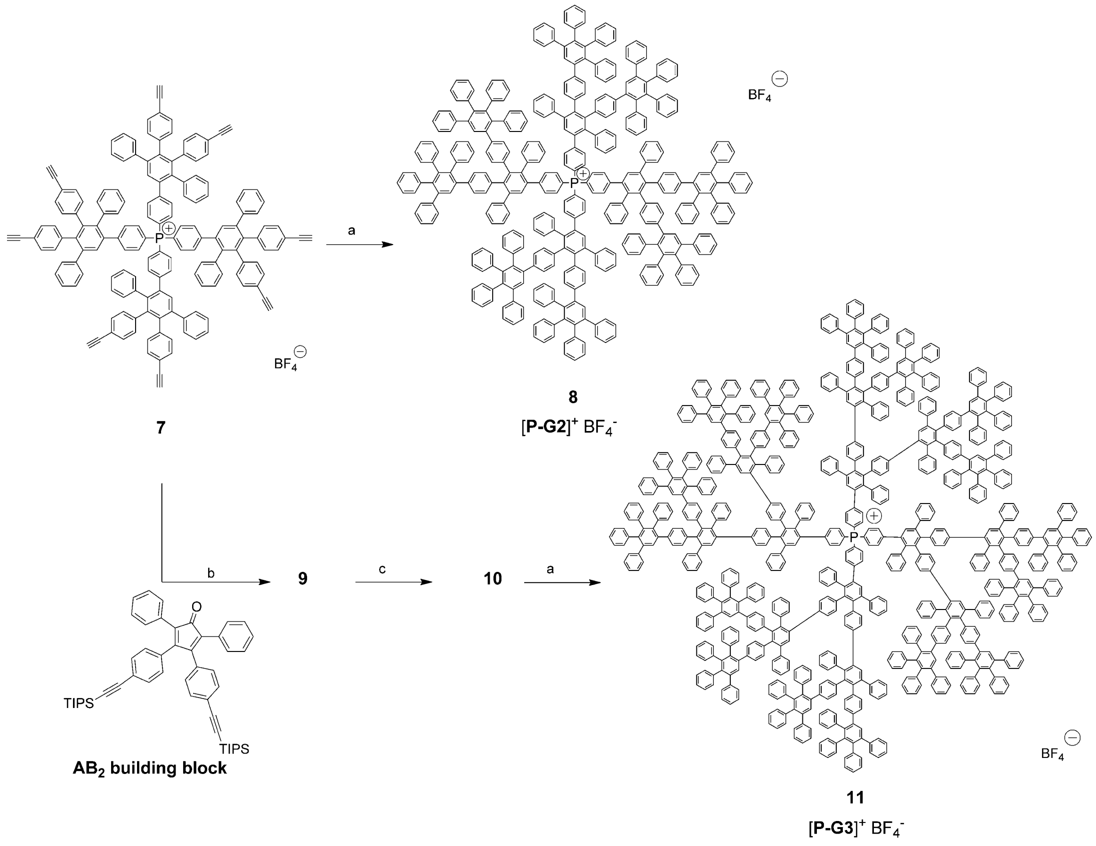


**Scheme 1.** Synthetic route to first-generation dendronized phosphonium cations: a) Mg, THF, $PCl_3$ (2.0 M in $CH_2Cl_2$), RT, overnight, 79 %; b) $K_2CO_3$ in $CH_3OH$, RT, 3 h, 86 %; c) $BF_3$*$OEt_2$, *t*$BuNO_2$, $CH_2Cl_2$, −20 °C, 90 %; d) toluene, 65 °C, 67 %; e) tetraphenylcyclopentadienone or $AB_2$ building block, respectively, *o*-xylene, 165 °C, 12 h, 78 % (**5**), 73 % (**6**); f) TBAF, THF, −20 °C, 2 h,

**1** using $K_2CO_3$ in methanol, tris[4-(ethynyl)phenyl]phosphine (**2**) was obtained. The quarternization of **2** as the crucial synthetic step was accomplished with the highly electrophilic tetrafluoroborate diazonium salt **3**, which was obtained by reacting 4-ethynylaniline with *tert*-butyl nitrite similar to a literature procedure.[15]

The build-up of the polyphenylene dendrons proceeded by means of a Diels-Alder reaction between ethynyl-functionalized phosphonium core **4** and tetraphenylcyclopentadienone,[16] making sure to remove any oxygen source (air, water, peroxides) to prevent the formation of phosphine oxide. Thus, a first-generation phosphonium tetrafluoroborate (**5**) was obtained in 78 % yield after purification by column chromatography and precipitation in hexane. MALDI-TOF mass spectrometry (single peak at *m/z* 1860.1), NMR measurements (for full characterization see the Supporting Information), and a single-crystal structure clearly showed the formation of a monodisperse first-generation phosphonium cation **5**.

The divergent dendritic growth was further exploited in order to construct even larger and more sterically shielded phosphonium structures (see Scheme 2, compounds **8** and **11**). The completion of the reactions was monitored by means of MALDI-TOF spectrometry (*m/z* 4904.9 showed formation of **8** and *m/z* 10987.9 of **11** accordingly, a full characterization of the isolated compounds is provided in Supporting Information).



**Scheme 2.** Synthetic route to higher generations of dendronized phosphonium cations: a) tetraphenylcyclopentadienone, *o*-xylene, 165 °C, 12 h, 61 % (**8**), 58 % (**11**); b) $AB_2$ building block, *o*-xylene, 165 °C, 36 h, 67 %; c) TBAF, THF, −20 °C, 2 h, 77 %.

77 %.

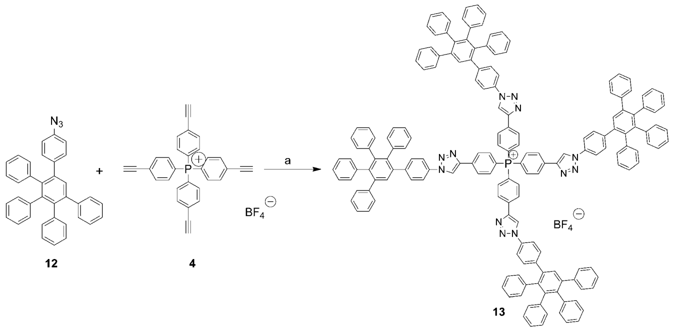
The hydrodynamic radii of the herein reported dendrimers were calculated from experimental diffusion coefficients ($D^{\mathrm{exptl}}$) measured by DOSY-NMR experiments ($CD_2Cl_2$, 298 K) and are summarized in Table 1.

**Table 1.** Diffusion coefficients, hydrodynamic radii and diameters of dendronized phosphonium salts **5**, **8** and **11** obtained from DOSY-NMR experiments ($CD_2Cl_2$, 298 K, 500 MHz).

| | $D^{\mathrm{exptl}}$ [$m^2 s^{-1}$] | Hydrodynamic radius $r_H$ [nm] | diameter [nm] |
|---|---|---|---|
| **5**, [**P-G1**]$^+BF_4^-$ | $4.07\times10^{-10}\pm1.05\times10^{-10}$ | 1.2±0.2 | 2.4±0.4 |
| **8**, [**P-G2**]$^+BF_4^-$ | $2.82\times10^{-10}\pm3.44\times10^{-11}$ | 1.8±0.2 | 3.5±0.4 |
| **11**, [**P-G3**]$^+BF_4^-$ | $2.04\times10^{-10}\pm4.7\times10^{-11}$ | 2.4±0.2 | 4.9±0.4 |

### Synthesis of a triazole-rich phosphonium cation

To avoid side products such as phosphine oxides, a dendrimer growth proceeding at lower temperatures and milder reaction conditions was needed. Therefore, a dendritic framework, comprising phenyl and triazolyl rings, was constructed by reacting bulky polyphenylene azide **12** (synthesis see Supporting Information) with ethynyl-functionalized tetraphenylphosphonium core **4** in a copper(I)-catalyzed dipolar 1,3-cycloaddition[17] (Scheme 3). The crude product **13** could be easily purified by column chromatography. This was attributed to its enhanced solubility in organic solvents ($CH_2Cl_2$, THF, $CH_3CN$) compared to recently reported triazole-rich polyphenylene dendrimers.[18]



**Scheme 3.** Synthetic route to first-generation phosphonium salt **13**: a) $CH_3CN$/THF 5:1, $CuSO_4$, Na-ascorbate, $NEt_3$, TBTA, 23 °C, 12 h, 87%.

$^1H$ NMR signals of the pure product **13** (87% yield) could be assigned and were used to confirm complete conversion, purity and regioselectivity (spectra see Supporting Information) in combination with MALDI-TOF analysis (*m/z* 2434.1).

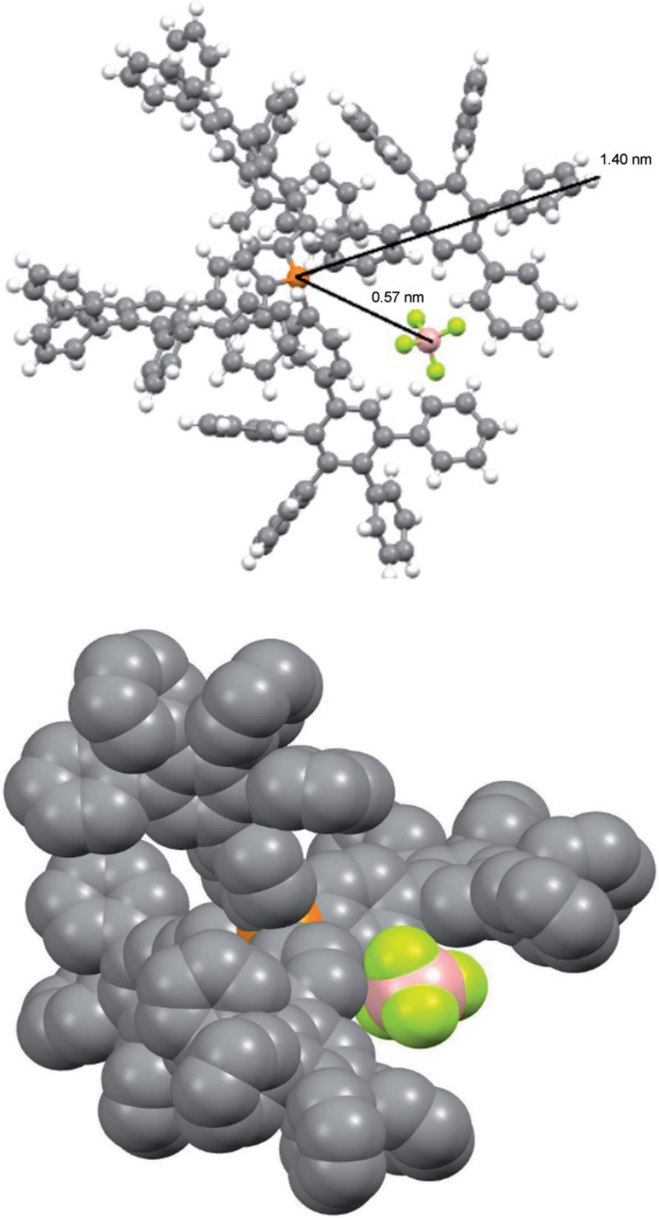


**Figure 1.** Left: Single-crystal structure of G1-phosphonium tetrafluoroborate **5** (solvents are omitted for clarity). Right: space-filling structure of **5**.

### Crystal structure of first-generation (G1) phosphonium tetrafluoroborate (5)

Yellow needles of **5** (or [**P-G1**]$^+BF_4^-$) were obtained from a $CH_2Cl_2$/hexane solution by slow evaporation at room temperature. The first-generation phosphonium salt crystallized in the tetragonal space group $I4_1/a$. Figure 1shows the single-crystal X-ray structure of **5**. The central P atom occupies the spatial position (0 1/4 1/8)—this means the four polyphenylene ligands are equivalent. The angles between the least-square planes of the phenyl ring with respect to the central ring varied from 57.0 to 63.6°.

The impact of dendronization on charge separation in the solid state can be reflected by the closest distance between cation and anion. In the single crystal of **5**, the distance from the boron atom in $BF_4^-$ to the central cationic phosphorus atom is 0.57 nm. Thus, the anion undergoes a significant interdigitation into the cavities of the hydrophobic polyphenylene scaffold due to Coulombic attraction. This becomes evident from the cation radius of **5** (1.40 nm, see Figure 1).

## Chemical and physical properties of hydrophobic phosphonium salts

At first the chemical stability of **5** (or [**P-G1**]$^{+}$$BF_4^{-}$) compared to non-dendronized tetraphenylphosphonium ($PPh_4^{+}Br^{-}$) with regard to alkaline decomposition in solution was investigated in a series of $^{31}$P NMR kinetic studies at 25 and 60 °C. The initial $PR_4^{+}$ species (0.1 м) was reacted at a tenfold molar excess with hydroxide ions (0.01 м), so that the degradation follows pseudo-second-order kinetics.[19] The rate constants $k$, the half-life times ($t_{1/2}$) and the activation energies ($E_A$) are reported in Table 2.

**Table 2.** Kinetic parameters for the alkaline degradation reaction of $PR_4^{+}$ $X^{-}$obtained from $^{31}$P NMR measurements assuming pseudo-second-order; $c_0(PR_4^{+})=0.1$ м; $c(OH^{-})=0.01$ м; a series of experiments was performed in DMF/$D_2O$ (9:1, v/v) over 24 h. Details see Supporting Information.

| Phosphonium salt | $T$ [°C] | $k$ [L mol$^{-1}$ h$^{-1}$] | $t_{1/2}$ [h] | $E_A$ [kJ mol$^{-1}$] |
|---|---|---|---|---|
| $PPh_4^{+}$ $Br^{-}$ | 25 | 0.19 ± 0.02 | 52.8 ± 6.6 | 35.0 ± 3.0 |
| | 60 | 0.84 ± 0.08 | 11.9 ± 1.1 | |
| dendrimer [**P-G1**]$^{+}$$BF_4^{-}$ | 25 | 0.08 ± 0.01 | 122.5 ± 17.9 | 45.6 ± 3.0 |
| | 60 | 0.52 ± 0.02 | 19.4 ± 0.9 | |

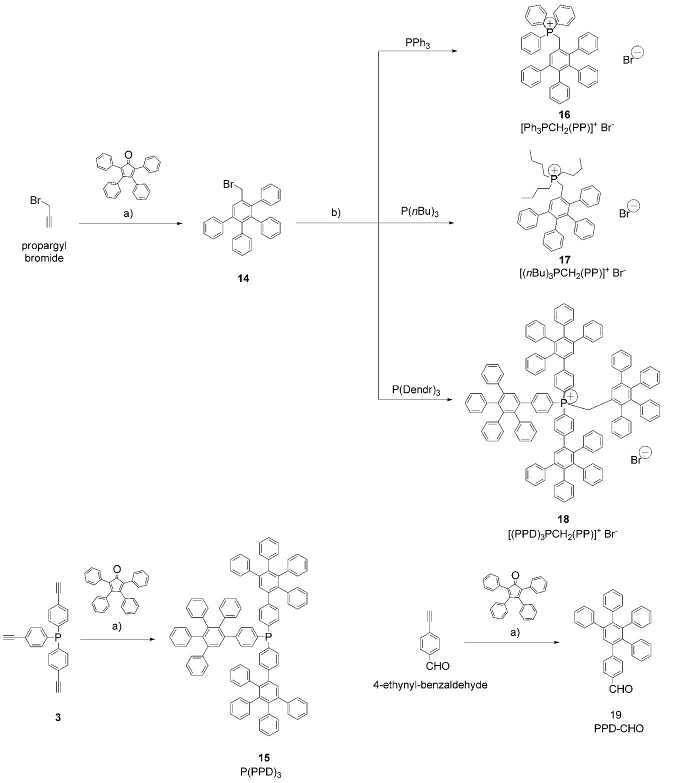
It is known from literature that common alkylphosphonium salts decompose rapidly under basic conditions (half-lives of minutes) by means of an ylide mechanism yielding phosphine oxides and hydrocarbons.[20] The obtained data indicate that base-stability is increased for the phosphonium dendrimer **5** ($t_{1/2}=122.5\pm17.9$ h, 25 °C), in comparison to non-dendronized $PPh_4^{+}Br^{-}$ ($t_{1/2}=52.8\pm6.6$ h, 25 °C).

In contrast to that, a neutral solution of dendronized salt **5** (non-degassed *o*-xylene, stirred in a sealed vial) exhibited temperature stability up to 120 °C without any decomposition (for at least three days). After additional refluxing (150 °C) for three weeks, $^{31}$P NMR analysis showed a conversion to phosphine oxide below 20 %. The thermal stability of G1-dendrimer **5** in the solid state was investigated by means of thermogravimetric analysis (TGA). The temperature range for decomposition under nitrogen-stream was found to be 350–360 °C, but TGA performed under air-stream essentially provided the identical result.

By combining increased chemical stability and ion dissociation,[21] dendritic encapsulated phosphonium salts represent an effective modulation of essential properties for the development of advanced hydroxide exchange membranes (HEMs).[22]

## Wittig ylides with bulky substituents around the phosphorus

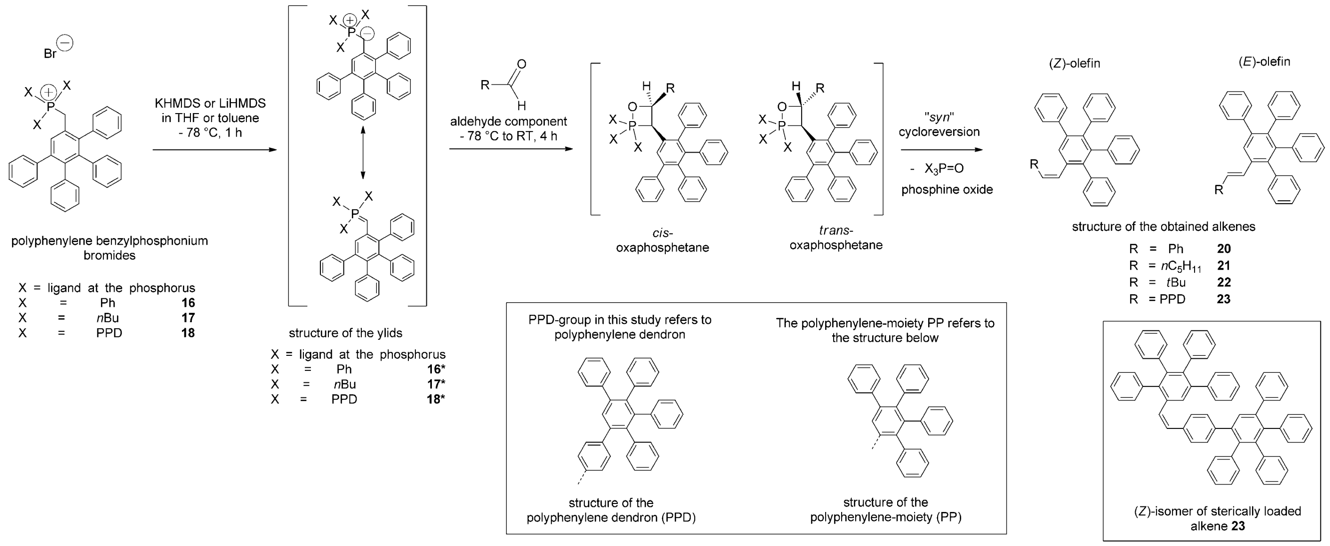
The synthesis of novel benzylphosphonium bromides **16**–**18** with unprecedentedly large polyphenylene substituents in α-position was achieved by a $S_N2$-type reaction between phosphines with first-generation benzylbromide derivative **14**. The advantages of the quarternization step are high product yields (> 90 %), easy purification, incorporation of an α-methylene-group, and the tailor-made arrangement of differently sized ligands X (Scheme 4) around the cationic phosphorus center. The bulky polyphenylene phosphine **15** ($P(PPD)_3$), readily reacted with **14** to yield fully dendronized phosphonium bromide **18** ($[(PPD)_3PCH_2(PP)]^{+}$ $Br^{-}$, see Scheme 4).



**Scheme 4.** Synthetic route to benzylphosphonium bromides **16**–**18**, as well as intermediates $P(PPD)_3$ **(15)** and PPD-CHO **(19)**: a) *o*-xylene, 155 °C, 12 h, 100 % ($PP-CH_2Br$), 69 % ($P(PPD)_3$); 89 % (PPD-CHO) b) $CH_3CN$, 60 °C, 12 h, 90–96 % yield.

The stereochemistry of the Wittig olefination in the presence of bulky α-substituents was investigated. Therefore, the formation of bulky, semi-stabilized ylides $Ph_3P{=}CH$-PP (**16***) and ($n$$Bu_3$)P=CH-PP (**17***) and the sterically completely shielded ylide $(PPD)_3P{=}CH$-PP (**18***) was initiated by treatment of the according benzylphosphonium bromide with potassium hexamethyldisilazide (KHMDS, salt-free conditions) and LiHMDS (lithium halide present) as bases at −78 °C (THF or toluene). After addition of aldehydes (benzaldehyde, hexanal, pivaldehyde and polyphenylene benzaldehyde derivative PPD-CHO **19)** to the ylide suspensions, the (*E/Z*) ratio of the obtained alkenes was determined from the coupling constant of the two vinylic protons (reaction conditions see Scheme 5, results see Table 3). Typical $^{3}J_{HH}$-values for the (*E*)-olefins were observed to be 16–17 Hz and 11-12.5 Hz for the (*Z*)-olefins, which is in agreement with experimental data of unsymmetrical substituted stilbenes.[23]

In salt-free Wittig reactions, semi-stabilized ylides usually react unselectively with aldehydes to yield (*E*)- and (*Z*)-alkenes.[11a] Our results revealed the exclusive formation of (*Z*)-ole-



**Scheme 5.** Reaction conditions, intermediates and final products of the Wittig reaction between benzylphosphonium bromides **16**–**18** and aldehydes R-CHO.

**Table 3.** Results of the Wittig reactions[a] according to Scheme 5.

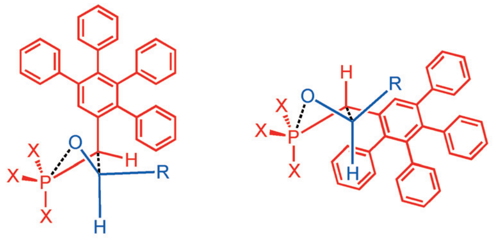
| | Phosphonium ylide $L_3P{=}CHPP$ | Base | Solvent | Aldehyde | (*E*/*Z*) ratio | Lit. (*E*/*Z*) ratio for $R'{=}CH_3$ | Isolated yield[b] [%] |
|---|---|---|---|---|---|---|---|
| [$Ph_3P{=}CH$-PP] (**16***) | | | | | | | |
| 1 | L = Ph | LiHMDS | THF | PhCHO | 1/99 | 17/83[11a] | 84 |
| 2 | L = Ph | LiHMDS | toluene | PhCHO | 1/99 | | 82 |
| 3 | L = Ph | KHMDS | THF | PhCHO | 1/99 | 8/92[14] | 63 |
| 4 | L = Ph | LiHMDS | THF | *n*-$C_5H_{11}CHO$ | 50/50 | 14/86[11a] | 78 |
| 5 | L = Ph | KHMDS | THF | *n*-$C_5H_{11}CHO$ | 40/60 | 6/94[14a] | 61 |
| 6 | L = Ph | LiHMDS | THF | $(CH_3)_3CCHO$ | 37/63 | | 82 |
| 7 | L = Ph | LiHMDS | toluene | $(CH_3)_3CCHO$ | 41/59 | | 80 |
| 8 | L = Ph | KHMDS | THF | $(CH_3)_3CCHO$ | n.d. | 1/99[11a] | 0[c] |
| 9 | L = Ph | LiHMDS | THF | PPD-CHO | 1/99 | | 74 |
| 10 | L = Ph | LiHMDS | toluene | PPD-CHO | 1/99 | | 70 |
| 11 | L = Ph | KHMDS | THF | PPD-CHO | 1/99 | | 59 |
| [*n*-$Bu_3P{=}CH$-PP (**17***) | | | | | | | |
| 12 | L = *n*Bu | LiHMDS | THF | PhCHO | 1/99 | | 88 |
| 13 | L = *n*Bu | LiHMDS | toluene | PhCHO | 1/99 | | 84 |
| 14 | L = *n*Bu | KHMDS | THF | PhCHO | 1/99 | 83/17[11a] | 76 |
| 15 | L = *n*Bu | LiHMDS | THF | *n*-$C_5H_{11}CHO$ | 72/28 | | 83 |
| 16 | L = *n*Bu | KHMDS | THF | *n*-$C_5H_{11}CHO$ | 85/15 | 67/33[11a] | 71 |
| 17 | L = *n*Bu | LiHMDS | THF | $(CH_3)_3CCHO$ | 81/19 | | 69 |
| 18 | L = *n*Bu | KHMDS | THF | $(CH_3)_3CCHO$ | 71/29 | 90/10[11a] | 64 |
| 19 | L = *n*Bu | LiHMDS | THF | PPD-CHO | 1/99 | | 86 |
| 20 | L = *n*Bu | LiHMDS | toluene | PPD-CHO | 1/99 | | 76 |
| 21 | L = *n*Bu | KHMDS | THF | PPD-CHO | 1/99 | | 59 |
| sterically shielded ylide [$PPD_3P{=}CH$-PP] (**18***) | | | | | | | |
| 22 | L = PPD | LiHMDS | THF | PhCHO | 1/99 | | 62 |
| 23 | L = PPD | LiHMDS | THF | *n*-$C_5H_{11}CHO$ | 52/48 | | 55 |

[a] Exact reaction procedure is described in Supporting Information. [b] After purification and isolation via column chromatography. [c] Product **31** was isolated in 86 % yield (structure see reaction scheme in Figure 15 in the Supporting Information). [d] Polyphenylene aldehyde **19** (PPD-CHO) was synthesized to incorporate an uncommonly large substituent at the aldehyde (Scheme 5). [e] Given that $CH_3$-groups in the α-position were not found in the literature, the shortest primary alkyl-chain analogue was selected.

fins when aromatic aldehydes (benzaldehyde, PPD-CHO **19**) are reacted with bulky, semi-stabilized ylide $Ph_3P{=}CH$-PP (**16***). Even the presence of $Li^+$ ions ($c = 0.05$ M) and the use of non-polar toluene as solvent did not affect the (*Z*)-selectivity (see entries 1–3, 9–11). Stabilized ylides are generally known to result in the preferential formation of (*E*)-alkenes.[11a,14a] Likewise the Wittig reaction of the ylide *n*$Bu_3P{=}CH$-PP (**17***) with hexanal and pivaldehyde predominantly yielded (*E*)-alkenes **21** and **22** (see entries **15**–**18**); however, upon reacting with benzaldehyde and PPD-CHO **19**, exclusively (*Z*)-alkenes **20** and **23** were obtained.

It is known that *cis*- or *trans*-disubstituted oxaphosphetanes represent the initially formed intermediates for the reaction between phosphorus ylides and aldehydes.[14a] The *cis*/*trans* ratio depends on the size and spatial arrangement of the substituents at the phosphorus. Inspired by the non-planar cycloaddition mechanism proposed by Vedejs et al.,[14b] we suggest the most likely transition state geometries in Figure 2.[24]

For the *cis*-configuration **24**, the group R of the aldehyde aligns in a pseudo-equatorial position in order to minimize destabilizing steric repulsion from the bulky PP dendron. For the case of the *trans*-orientation **25**, however, the group R encounters even more unfavorable steric interaction with the PP moiety, since both large groups are arranged in the pseudo-equatorial plane.



**24**
*cis*-oxaphosphetane
transition state

**25**
*trans*-oxaphosphetane
transition state

**Figure 2.** Proposed transition state geometries for Wittig reactions between polyphenylene ylides (**16***–**18***, red) and aldehyde RCHO (blue).

## Conclusion

We have presented the synthesis of rigid, bulky, and hydrophobic polyphenylene phosphonium cations by divergent dendritic growth through a thermal Diels–Alder cycloaddition. The use of an organic diazonium salt enabled the synthesis of the functionalized phosphonium core **4**, which has not been reported before, and provided the tetrahedral branching unit for the subsequent synthesis of dendrimers. In addition to that, an improved S$_N$2-type method for the quarternization reaction of phosphines was employed to prepare benzylphosphonium bromides with unprecedented large and rigid $\alpha$-substituents.

Stability investigations by means of $^{31}$P NMR kinetic studies revealed that the dendritically shielded phosphonium cation [**P-G1**]$^+$ (first-generation) undergoes a remarkably slower degradation to phosphine oxide in alkaline solution compared to the non-dendronized tetraphenylphosphonium cation [PPh$_4$]$^+$.

The application of the benzylphosphonium bromides as Wittig precursors resulted in the formation of encapsulated phosphorus ylides, which were further reacted with aldehydes to yield novel olefins with bulky substituents. The stereochemical analysis of the obtained alkenes showed the exclusive formation of (*Z*)-isomers when aromatic aldehydes were employed. For the first time, we report a successful preparation of the sterically congested polyphenylene (*Z*)-stilbene derivative **23**. This work will enable further research on its structure[25] and related rotational barriers.[26] Additionally, conformational differences between the ground state and excited state may be investigated, since even less hindered stilbenes are known to exhibit unusual Stokes Shifts in fluorescence emission spectra.[27] Moreover, the photocyclization of (*Z*)-stilbene **23** to conformationally strained dihydrophenanthrene intermediates[28] has to be elucidated. Finally, the applicability of organic photoisomers for energy storage[29] based on polyphenylene stilbene derivatives will be discussed in future studies.

## Experimental Section

Experimental details are provided in the Supporting Information.

## Acknowledgements

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**Keywords:** phosphonium salts · phosphorus · polyphenylene olefins · weakly coordinating cations · Wittig reactions · ylides

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