

Phosphorus Copies of PPV: π -Conjugated Polymers and Molecules Composed of Alternating Phenylene and Phosphaalkene Moieties

Vincent A. Wright, Brian O. Patrick, Celine Schneider, and Derek P. Gates*

Contribution from the Department of Chemistry, University of British Columbia,
2036 Main Mall, Vancouver, British Columbia, Canada V6T 1Z1

Received February 10, 2006; Revised Manuscript Received April 26, 2006; E-mail: dgates@chem.ubc.ca

Abstract: A new class of π -conjugated macromolecule, poly(*p*-phenylenephosphaalkene) (**PPP**), is reported. **PPPs** are phosphorus analogues of the important electronic material poly(*p*-phenylenevinylene) (**PPV**) where P=C rather than C=C bonds space phenylene moieties. Specifically, **PPPs** [$-\text{C}_6\text{R}_4-\text{P}=\text{C}(\text{OSiMe}_3)-\text{C}_6\text{R}'_4-\text{C}(\text{OSiMe}_3)=\text{P}-$] $_n$ (**1**: R = H, R' = Me; **11**: R = Me, R' = H) were synthesized by utilizing the Becker reaction of a bifunctional silylphosphine, 1,4- $\text{C}_6\text{R}_4[\text{P}(\text{SiMe}_3)_2]_2$, and diacid chloride 1,4- $\text{C}_6\text{R}'_4[\text{COCI}]_2$. Several model compounds for **PPP** are reported. Namely, mono(phosphaalkene)s $\text{R}-\text{P}=\text{C}(\text{OSiMe}_3)-\text{R}'$ (**4**: R = Ph, R' = Mes; **7**: R = Mes, R' = Ph), C-centered bis(phosphaalkene)s $\text{R}-\text{P}=\text{C}(\text{OSiMe}_3)-\text{C}_6\text{R}'_4-\text{C}(\text{OSiMe}_3)=\text{P}-\text{R}$ (**5**: R = Ph, R' = Me; **8**: R = Mes, R' = H), and P-centered bis(phosphaalkene)s $\text{R}-\text{C}(\text{OSiMe}_3)=\text{P}-\text{C}_6\text{R}'_4-\text{P}=\text{C}(\text{OSiMe}_3)-\text{R}$ (**6**: R = Mes, R' = H; **10**: R = Ph, R' = Me). Remarkably, selective *Z*-isomer formation (i.e., trans arylene moieties) is observed for **PPPs** when bulky P-substituents are employed while *E/Z*-mixtures are otherwise obtained. X-ray crystal structures of **Z-7**, **Z,Z-8**, and **Z,Z-10** suggest moderate π -conjugation. The twist angles between the P=C plane and unsubstituted arenes are 16° – 26° , while those between the P=C plane and methyl-substituted arenes are 59° – 67° . The colored **PPPs** and their model compounds were studied by UV/vis spectroscopy, and the results are consistent with extended π -conjugation. Specifically, weakly emissive polymer **E/Z-1** ($\lambda_{\text{max}} = 338$ nm) shows a red shift in its absorbance from model **E/Z-4** ($\lambda_{\text{max}} = 310$ nm), while a much larger red shift is observed for **Z-11** ($\lambda_{\text{max}} = 394$ nm) over **Z-7** ($\lambda_{\text{max}} = 324$ nm).

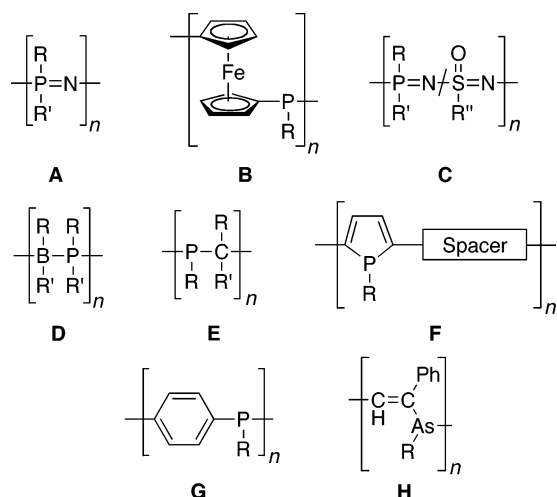
Introduction

The development of new polymers incorporating inorganic elements into the main chain is a challenging research frontier that promises to lead to materials with exciting properties and possible specialty applications.^{1,2} Inorganic macromolecules composed of phosphorus atoms in the backbone have attracted considerable attention with the polyphosphazenes (**A**) being the most important class (see Chart 1).³ Recently, major advances in the breadth of phosphorus polymer chemistry have been made including the synthesis of poly(ferrocenylphosphine)s (**B**),⁴ polythionylphosphazenes (**C**),⁵ polyphosphinoboranes (**D**),⁶ and poly(methylenephosphine)s (**E**).⁷ In the past few years, there

has been a growth of activity in π -conjugated phosphorus macromolecules because of their potential electronic applications.⁸ Perhaps the most thoroughly investigated of these are the polyphospholes. Although the parent polyphosphole is not known, several oligomeric and polymeric species containing phospholes have been reported (**F**).^{9–18} The fabrication of the

- (1) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*, 2nd ed.; Oxford University Press: 2005.
- (2) Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1603–1621.
- (3) Allcock, H. R. *Chemistry and Applications of Polyphosphazenes*; John Wiley & Sons: New Jersey, 2003.
- (4) See, for example: Withers, H. P.; Seyferth, D. *Organometallics* **1982**, *1*, 1275–1282. Withers, H. P.; Seyferth, D. *Organometallics* **1982**, *1*, 1283–1288. Honeyman, C. H.; Foucher, D. A.; Dahmen, F. Y.; Rulkens, R.; Lough, A. J.; Manners, I. *Organometallics* **1995**, *14*, 5503–5512. Honeyman, C. H.; Peckham, T. J.; Massey, J. A.; Manners, I. *Chem. Commun.* **1996**, 2589–2590. Peckham, T. J.; Massey, J. A.; Honeyman, C. H.; Manners, I. *Macromolecules* **1999**, *32*, 2830–2837.
- (5) See, for example: McWilliams, A. R.; Gates, D. P.; Edwards, M.; Liable-Sands, L. M.; Guzei, I.; Rheingold, A. L.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 8848–8855. Chunechom, V.; Vidal, T. E.; Adams, H.; Turner, M. L. *Angew. Chem., Int. Ed.* **1998**, *37*, 1928–1930. Gates, D. P.; McWilliams, A. R.; Manners, I. *Macromolecules* **1998**, *31*, 3494–3497. Liang, M.; Manners, I. *J. Am. Chem. Soc.* **1991**, *113*, 4044–4045.

- (6) See, for example: Dorn, H.; Singh, R. A.; Massey, J. A.; Lough, A. J.; Manners, I. *Angew. Chem., Int. Ed.* **1999**, *38*, 3321–3323. Dorn, H.; Singh, R. A.; Massey, J. A.; Nelson, J. M.; Jaska, C. A.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 6669–6678. Dorn, H.; Rodezno, J. M.; Brunnhöfer, B.; Rivard, E.; Massey, J. A.; Manners, I. *Macromolecules* **2003**, *36*, 291–297. Denis, J.-M.; Forintos, H.; Szelke, H.; Toupet, L.; Pham, T.-N.; Madec, P.-J.; Gaumont, A.-C. *Chem. Commun.* **2003**, 54–55. Clark, T. J.; Rodenzo, J. M.; Clendenning, S. B.; Aouba, S.; Brodersen, P. M.; Lough, A. J.; Ruda, H. E.; Manners, I. *Chem.—Eur. J.* **2005**, *11*, 4526–4534.
- (7) Tsang, C.-W.; Yam, M.; Gates, D. P. *J. Am. Chem. Soc.* **2003**, *125*, 1480–1481.
- (8) Hissler, M.; Dyer, P.; Réau, R. *Coord. Chem. Rev.* **2003**, *244*, 1–44.
- (9) Deschamps, E.; Ricard, L.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1158.
- (10) Mao, S. S. H.; Tilley, T. D. *Macromolecules* **1997**, *30*, 5566–5569.
- (11) Hay, C.; Fischmeister, C.; Hissler, M.; Toupet, L.; Réau, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 1812–1815.
- (12) Hay, C.; Hissler, M.; Fischmeister, C.; Rault-Berthelot, J.; Toupet, L.; Nyulászi, L.; Réau, R. *Chem.—Eur. J.* **2001**, *7*, 4222–4236.
- (13) Morisaki, Y.; Aiki, Y.; Chujo, Y. *Macromolecules* **2003**, *36*, 2594–2597.
- (14) Hay, C.; Fave, C.; Hissler, M.; Rault-Berthelot, J.; Réau, R. *Org. Lett.* **2003**, *5*, 3467–3470.
- (15) Fave, C.; Hissler, M.; Kárpáti, T.; Rault-Berthelot, J.; Deborde, V.; Toupet, L.; Nyulászi, L.; Réau, R. *J. Am. Chem. Soc.* **2004**, *126*, 6058–6063.
- (16) Baumgartner, T.; Neumann, T.; Wirges, B. *Angew. Chem., Int. Ed.* **2004**, *43*, 6197–6201.
- (17) Neumann, T.; Dienes, Y.; Baumgartner, T. *Org. Lett.* **2006**, *8*, 495–497.

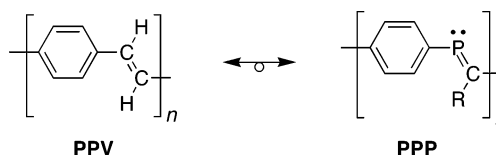
Chart 1. Selected Examples of Polymers Containing Group 15 Elements in the Main Chain

first organophosphorus-based LEDs using oligophospholes represents an exciting recent achievement in this field.^{19,20} Novel phosphorus analogues of polyaniline have been prepared, and these poly(*p*-phenylenephosphine)s (**G**) possess electronic properties that are consistent with extended π -conjugation.^{21–23} Although the phosphorus analogue has not been reported, it is worth noting that luminescent poly(vinylene arsines) (**H**) have also been prepared.^{24–26} Many of the aforementioned polymers contain pyramidal phosphorus atoms. We postulated that more effective π -conjugation might be observed if the phosphorus atoms were directly involved in (p– π) bonding by incorporating P=C bonds into the polymer structure.

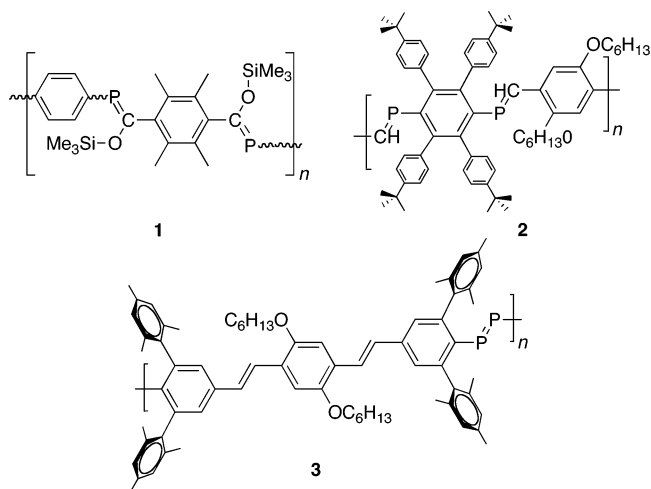
The investigation of compounds possessing heavy element (*np–mp*) π bonds ($n > 2$; $m \geq 2$) continues to be an important central theme in main group chemistry.²⁷ These low-coordinate species pose a considerable synthetic challenge yet are attractive because their intriguing structural features challenge our understanding of chemical bonding^{28,29} and offer a means to expand the diverse chemistry of olefins and alkynes to other systems.^{30,31} This year marks the thirtieth anniversary of the landmark development of the first isolable phosphalkenes by Becker³² and the detection of the parent HP=CH₂ by Kroto and Nixon.³³ Conceptually, a phosphalkene is derived by replacing one of the methylene fragments (R₂C) of an alkene with the isolobal phosphinidene (RP) group. The development of phosphalkenes has unveiled a fertile new area of phosphorus chemistry and has played a major role in low-coordinate

phosphorus being coined “the carbon copy”.^{31,34,35} The parallels between phosphalkenes and alkenes are evidenced by the occurrence of phospho-variants of reactions common for olefins such as Peterson and Wittig olefination, 1,2-addition, [4+2] cycloaddition, η^2 metal coordination, and Cope and allylic rearrangements.

Our research group is interested in expanding the phosphorus–carbon analogy to polymer science and has been utilizing the isolobal relationship between P=C and C=C bonds. To this end, we recently reported the successful polymerization of a P=C bond, by analogy with olefin polymerization, to afford poly(methylenephosphine) (**E**, Chart 1).⁷ The preparation of macromolecules where the P=C bond is directly incorporated into the backbone is also of considerable interest.³⁶ The formal replacement of the C=C moiety by a P=C moiety in the important organic π -conjugated polymer poly(*p*-phenylenevinylene) (PPV)³⁷ would result in a poly(*p*-phenylenephosphalkene) (PPP) and is expected to lead to a new generation of electronic materials. Moreover, the successful preparation of



PPPs, although synthetically challenging, would provide a unique opportunity to further investigate the parallel between P=C and C=C bonds. The first examples of PPPs (**1** and **2**) have recently been reported by us³⁸ and Protasiewicz.^{39–41} These phosphalkene-containing polymers, as well as the diphosphene-containing polymer **3**,⁴⁰ exhibit electronic properties consistent with extended π -conjugation in the main chain.



Herein, we report our detailed studies of PPPs, phosphorus copies of PPV, including their synthesis, electronic properties,

- (18) Baumgartner, T.; Wilk, W. *Org. Lett.* **2006**, *8*, 503–506.
 (19) Fave, C.; Cho, T.-Y.; Hissler, M.; Chen, C.-W.; Luh, T.-Y.; Wu, C.-C.; Réau, R. *J. Am. Chem. Soc.* **2003**, *125*, 9254–9255.
 (20) Su, H.-C.; Fadhei, O.; Yang, C.-J.; Cho, T.-Y.; Fave, C.; Hissler, M.; Wu, C.-C.; Réau, R. *J. Am. Chem. Soc.* **2006**, *128*, 983–995.
 (21) Lucht, B. L.; St. Onge, N. O. *Chem. Commun.* **2000**, 2097–2098.
 (22) Jin, Z.; Lucht, B. L. *J. Organomet. Chem.* **2002**, *653*, 167–176.
 (23) Jin, Z.; Lucht, B. L. *J. Am. Chem. Soc.* **2005**, *127*, 5586–5595.
 (24) Umeyama, T.; Naka, K.; Bravo, M. D.; Nakahashi, A.; Chujo, Y. *Polym. Bull.* **2004**, *52*, 191–199.
 (25) Umeyama, T.; Naka, K.; Chujo, Y. *Macromolecules* **2004**, *37*, 3623–3629.
 (26) Naka, K.; Umeyama, T.; Chujo, Y. *J. Am. Chem. Soc.* **2002**, *124*, 6600–6603.
 (27) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463–3504.
 (28) Power, P. P. *J. Chem. Soc., Dalton Trans.* **1998**, 2939–2951.
 (29) Power, P. P. *Chem. Commun.* **2003**, 2091–2101.
 (30) Mathey, F. *Acc. Chem. Res.* **1992**, *25*, 90–96.
 (31) Mathey, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1578–1604.
 (32) Becker, G. Z. *Anorg. Allg. Chem.* **1976**, *423*, 242–254.
 (33) Hopkinson, M. J.; Kroto, H. W.; Nixon, J. F.; Simmons, N. P. *C. J. Chem. Soc., Chem. Commun.* **1976**, 513–515.

- (34) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: West Sussex, 1998.
 (35) Regitz, M.; Scherer, O. J. *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Georg Thieme Verlag Thieme Medical Publishers: New York, 1990.
 (36) Recently, novel polymers have been reported where P=C bonds are incorporated into the side-group structure. See: Toyota, K.; Ujita, J.; Kawasaki, S.; Abe, K.; Yamada, N.; Yoshifuji, M. *Tetrahedron Lett.* **2004**, 7609–7612.
 (37) For reviews, see: (a) *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Dekker: New York, 1998. (b) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402–428.

Table 1. Selected Characterization Data for Model Compounds and Polymers

compound	δ P=C (ppm)		M_n (g/mol)	λ_{\max} (nm)	Z/E (%)	isolated yield (%)	reference
	^{31}P NMR	^{13}C NMR ^a					
4	134.0 (Z) 149.2 (E)	197.3 (Z, 49 Hz) 210.2 (E, 41 Hz)	328	310	46:54	75	this work
5	134.0, 131.8, 129.9, 129.6 (Z) 155.2, 154.9, 150.7, 149.5 (E)	198.6 (Z, 49 Hz) 211.8 (E, 44 Hz)	550	314	56:44	42	this work
6	132.3 (Z,Z) 148.3, 134.8 (E,Z) 149.2 (E,E)	195.5 (49 Hz) 209.7 (41 Hz) 210.4 (41 Hz)	578	332	12:88	54	this work
1 (trial 1)	132 (Z) 152 (E)	197.9 (Z) 211.9 (E)	2900 ^b	328	53:47	35	this work
1 (trial 2)			6300 ^b	334	51:49		this work
1 (trial 3)			6300 ^b	334	51:49		this work
1 (trial 4)			10 500 ^b	338	53:47		this work
7	141.5 (Z)	197.3 (Z, 56 Hz)	328	324	100:0	40	this work
8	146.3 (Z,Z)	196.4 (Z,Z, 60 Hz)	579	388	100:0	71	this work
10	150.2 (Z,Z)	195.9 (Z,Z, 55 Hz)	551	337	100:0	62	this work
11	153 (Z)	194 (Z)	N/A ^c	394 ^d	100:0	88	this work
12	141.3 (Z)	188.5 (Z, 52 Hz)	496	306	100:0		51
19	248.6 (E)	N/A	846	349	0:100		66
23	259.2 (E)	173.7 (E)	655	326	0:100		75, 76
25	243.5 (E)	N/A	790	411	0:100		39
26	243.3 (E)	N/A	991	445	0:100		39
2	250.5 (E), 270.6 (E)	N/A	6500	445	0:100		39

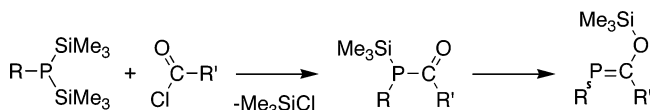
^a Our ^{13}C NMR assignments of the P=C carbon for *E*- and *Z*-isomers of **4**, **5**, and **1** were incorrect in ref 38. Reexamination of the spectra and comparison to that observed for *Z*-**7**, *Z*,*Z*-**8**, *Z*,*Z*-**10**, and *Z*-**11** led to this new assignment. ¹ $J_{\text{C}=\text{P}}$ is given in parentheses. ^b M_n was estimated using end group analysis. ^c Could not use end group analysis using CP-MAS NMR. ^d UV/vis spectroscopy performed on the THF soluble fraction of the mostly insoluble **11**.

and methods to control the stereochemistry of the P=C bond. As is common in the study of π -conjugated polymers,⁴² we have systematically prepared molecular model compounds for the polymer. Structural and spectroscopic investigations of these systems are consistent with extended π -conjugation between the P=C and phenylene moieties in the backbone of **PPP**.

Results and Discussion

When we embarked on this project, we realized that the biggest challenge to the preparation of a P=C analogue of **PPV** would lie in choosing the synthetic route. To achieve a satisfactory degree of polymerization through condensation polymerization, the phosphorus–carbon bond forming step must be quantitative and the monomers must be of very high purity.⁴³ Of the numerous routes known for the preparation of phosphoalkenes, the aforementioned Becker method (Scheme 1) attracted our attention since it is convenient, is high yielding,

Scheme 1. Becker Route to Phosphaalkenes: Condensation Followed by the [1,3]-Sigmatropic Rearrangement of an Acylphosphine to a Phosphaalkene



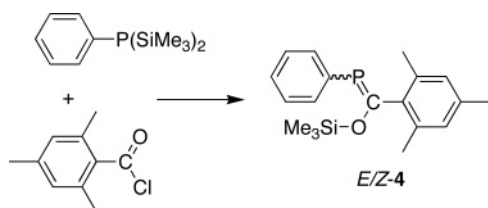
and tolerates a variety of substituents.⁴⁴ This reaction involves initial condensation of an acid chloride with a bis(trimethylsilyl)-phosphine to form a transient acylphosphine that rapidly tautomerizes to the phosphaalkene. Another attractive feature of the Becker route is that the sole byproduct (Me_3SiCl) is easily removed which simplifies polymer purification.

Synthesis and Characterization of Mixed E/Z-PPPs. The simplest model for **PPP** is $\text{PhP}=\text{C}(\text{OSiMe}_3)\text{Ph}$; however, previous studies showed that this compound is unstable and readily dimerizes.⁴⁵ We realized that steric protection would be necessary to stabilize the P=C bond. However, extremely bulky groups such as supermesityl ($\text{Mes}^* = 2,4,6\text{-tri-}t\text{-butylphenyl}$) would cause backbone twisting and, consequently, diminish π -conjugation. Therefore, the smaller mesityl substituent ($\text{Mes} = 2,4,6\text{-trimethylphenyl}$) was chosen for this task. To accurately model the backbone of the target polymer and to evaluate π -conjugation in the backbone, mono(phosphaalkene) (**4**) and two bis(phosphaalkene)s (**5** and **6**) were prepared. Important spectroscopic data for these model compounds are given in Table 1. Interestingly, the ^{31}P NMR spectrum of phosphaalkene **4** (yield = 75%) shows signals for both *E*- and *Z*-isomers (δ 149.2, 54%, *E*; 134.0, 46%, *Z*) assigned by

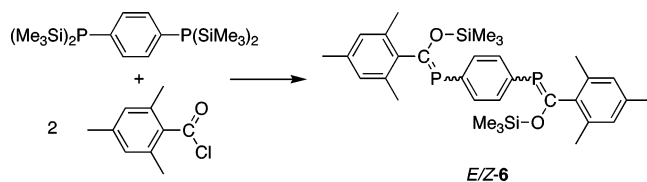
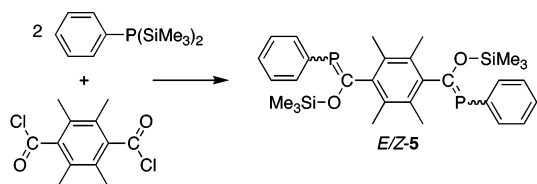
- (38) Wright, V. A.; Gates, D. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 2389–2392.
 (39) Smith, R. C.; Chen, X.; Protasiewicz, J. D. *Inorg. Chem.* **2003**, *42*, 5468–5470.
 (40) Smith, R. C.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **2004**, *126*, 2268–2269.
 (41) Smith, R. C.; Protasiewicz, J. D. *Eur. J. Inorg. Chem.* **2004**, 998–1006.
 (42) See, for example: van Hutten, P. F.; Hadziioannou, G. *Semiconducting Polymers* **2000**, 561–613. van Hutten, P. F.; Krasnikov, V. V.; Hadziioannou, G. *Acc. Chem. Res.* **1999**, *32*, 257–265. Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350–1377. Müllen, K.; Wegner, G., Eds. *Electronic Materials. The Oligomer Approach*; Wiley-VCH: New York, 1998. Tour, J. M. *Chem. Rev.* **1996**, *96*, 537–554. Müllen, K. *Pure Appl. Chem.* **1993**, *65*, 89–96.
 (43) In a step growth polymerization, the extent of reaction (p) determines the number-average degree of polymerization (X_n) according to the Carothers equation: $X_n = 1/(1-p)$. Therefore, to achieve a polymer with 100 repeat units, the reaction must proceed to 99% completion. In addition, stoichiometric imbalance ($r = N_A/N_B$; where $N_A = \text{mol of monomer A}$ and $N_B = \text{mol of monomer B}$) also leads to lower average degrees of polymerization according to the following equation: $X_n = (1+r)/(1+r-2rp)$. Stoichiometric imbalance may arise due to difficulty measuring accurate quantities of monomers or, more likely, the presence of impurities. For the aforementioned polymerization (two bifunctional monomers $\text{A-A} + \text{B-B}$) which proceeds to 99% completion, an imbalance in stoichiometry of 0.99 (i.e., a 1% excess of B–B) will decrease the degree of polymerization (X_n) from 100 to 67. For a nice discussion of the challenge of achieving high molecular weight using step polymerization, see: Odian, G. *Principles of Polymerization*; Wiley: New York, 1991; Chapter 2.

- (44) See, for example: (a) Becker, G. *Z. Anorg. Allg. Chem.* **1977**, *430*, 66–76. (b) Becker, G.; Mundt, O. *Z. Anorg. Allg. Chem.* **1978**, *443*, 53–69. (c) Becker, G.; Becker, W.; Uhl, G. *Z. Anorg. Allg. Chem.* **1984**, *518*, 21–35. (d) Pietschnig, R.; Niecke, E.; Nieger, M.; Airola, K. *J. Organomet. Chem.* **1997**, *529*, 127–133. (e) Gruenhagen, A.; Pieper, U.; Kottke, T.; Roesky, H. W. *Z. Anorg. Allg. Chem.* **1994**, *620*, 716–722. (f) Mack, A.; Pierron, E.; Allspach, T.; Bergsträber, U.; Regitz, M. *Synthesis-Stuttgart* **1998**, 1305–1313.
 (45) Becker, G.; Becker, W.; Mundt, O. *Phosphorus Sulfur* **1983**, *14*, 267–283.

comparison to similar phosphalkenes from the literature.^{32,46,47} The *E*-isomer features the two aryl substituents in *cis* positions, while in the *Z*-isomer the aryl groups are *trans* configured and this isomer is expected to be more π -conjugated.

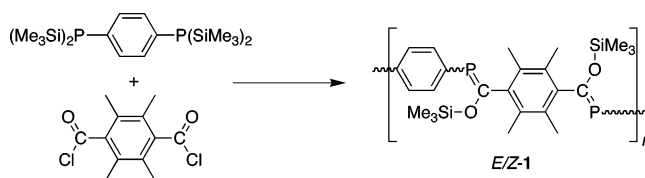


The bis(phosphaalkene)s (**5** and **6**) can be prepared quantitatively (by ³¹P NMR spectroscopy). However, these compounds are difficult to isolate as solids due to their high solubility in hexanes even at low temperatures, and consequently, low isolated yields are obtained (**5**, 42%; **6**, 54%). Similar to that observed for mono(phosphaalkene) **4**, the NMR spectra of bis-(phosphaalkene)s **5** and **6** indicate that a mixture of *E*- and *Z*-isomers is present. The ³¹P NMR spectrum of a bis-(phosphaalkene) should show four resonances [*E,E*- (1 signal); *Z,Z*- (1 signal); *E,Z*- (2 signals)]. As predicted, four signals are observed in the phosphaalkene region of the ³¹P NMR spectrum of **6** and are assigned as follows: *E,E*-**6** (δ 149.2, 78%), *E,Z*-**6** (δ 148.3, 134.8; 20%), and *Z,Z*-**6** (δ 132.3, 2%). These assignments were made on comparison with other phosphaalkenes prepared in this and previous studies.^{32,46,47} Unexpectedly, the ³¹P NMR spectrum of bis(phosphaalkene) **5** exhibits eight resonances distributed over the regions expected for *E*- (44%) and *Z*-phosphaalkene (56%) isomers. The presence of eight rather than four signals can be rationalized by assuming that the bulky C₆Me₄ spacer restricts free rotation of the P=C moieties. As a consequence, each isomer has *syn*- and *anti*-conformers, and the number of signals increases from four to eight. Presumably, the C₆H₄ central spacer in **6** does not hinder rotation of the P=C groups on the NMR time scale, and thus four signals are observed as expected. The UV/vis data (discussed below) also support this hypothesis since *E/Z*-**6** appears to be more π -conjugated than *E/Z*-**5**.

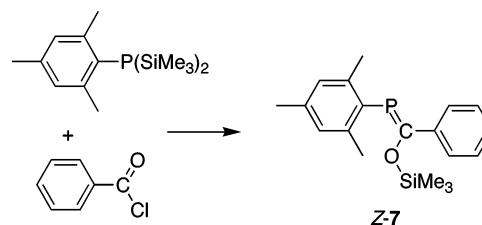


With model compounds *E/Z*-**4**, *E/Z*-**5**, and *E/Z*-**6** in hand, the target poly(*p*-phenylenephosphaalkene) (**1**) could be prepared. Heating the bifunctional carboxylic acid chloride and silylphos-

phine monomers in the melt (85 °C) affords **PPP** (**1**) as a viscous yellow gum. The ³¹P NMR spectrum of **1** shows broad overlapping signals assigned to *E*- and *Z*-configured P=C bonds and a sharp signal assigned to -P(SiMe₃)₂ end groups. Importantly, broad resonances at 212 and 198 ppm assigned to the vinylic carbons of the *E*- and *Z*-isomers are detected in the ¹³C{¹H} NMR spectrum of *E/Z*-**1**. Attempts to estimate the molecular weight of the poly(*p*-phenylenephosphaalkene) **1** by GPC and MALDI-TOF MS were precluded by the air and moisture sensitivity of the polymer. The relative integration of the -P(SiMe₃)₂ and P=C signals in the ³¹P NMR spectrum suggests that the number average molecular weights (*M*_n) for various samples of **1** range from 2900 to 10 500 g mol⁻¹ (see Table 1). The molecular weights determined by end group analysis match well with elemental analyses, including chlorine analysis. Unfortunately, attempts to obtain higher molecular weight **1** by heating for 48 h afford insoluble yellow-orange gels that swelled reversibly in THF. Nevertheless, the ³¹P NMR spectra of these swollen gels exhibit broad resonances similar to those for the soluble polymer *E/Z*-**1** suggesting that the gel is higher molecular weight or partially cross-linked *E/Z*-**1**.



Synthesis and Characterization of Z-PPPs. Thus far, we have shown that mixed *E/Z*-PPP and molecular models could be prepared; however, we sought an all *Z*-PPP which we anticipated would show more extensive π -conjugation. It has previously been noted that Becker phosphaalkenes show a preference for the *Z*-isomer when bulky P-substituents (i.e., ^tBu and Mes*) are employed.^{32,48} Therefore, we speculated that PPPs bearing bulky P-substituents would selectively form as *Z*-isomers, and we embarked on the preparation of the model compound **7**.



Previously unknown mono(phosphaalkene) **7** can be prepared by stirring MesP(SiMe₃)₂ and PhCOCl in THF for 1 d at 25 °C. Remarkably, only a single resonance in the phosphaalkene region (δ 141.5) is detected in the ³¹P NMR spectrum of the reaction mixture suggesting that, unlike *E/Z*-**4**, only one isomer of **7** is present. Additional evidence for the stereoselective formation of **7** is obtained from the relatively simple ¹³C{¹H} NMR spectrum. Notably, a distinctive doublet resonance is detected at 197.3 ppm (¹J_{PC} = 56 Hz) which can be assigned to the vinylic carbon of the *Z*-P=C isomer. In contrast to liquid *E/Z*-**4**, solid **7** is crystalline and the analysis of single crystals

(46) Becker, G.; Beck, H. P. *Z. Anorg. Allg. Chem.* **1977**, *430*, 77–90.

(47) Fluck, E. *Topics in Phosphorus Chemistry*; Wiley: New York, 1980; Vol. 10.

(48) Yoshifuji, M.; Toyota, K.; Inamoto, N. *Phosphorus Sulfur* **1985**, *25*, 237–243.

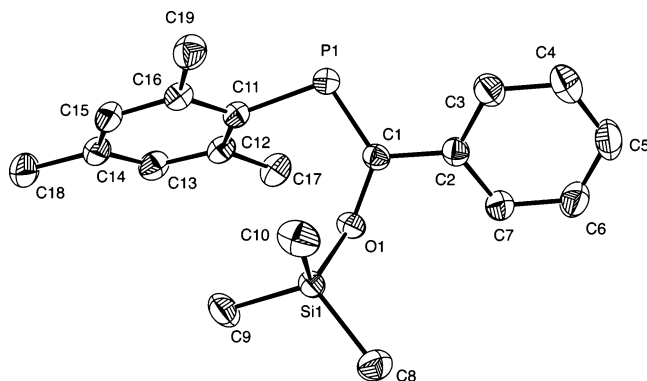


Figure 1. Molecular structure of **7** (50% probability). All hydrogen atoms are omitted for clarity.

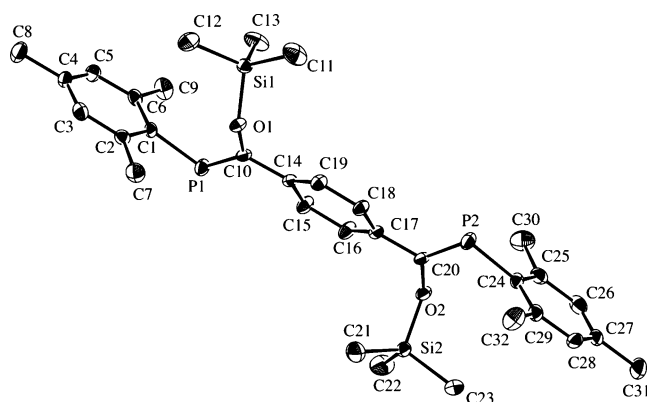
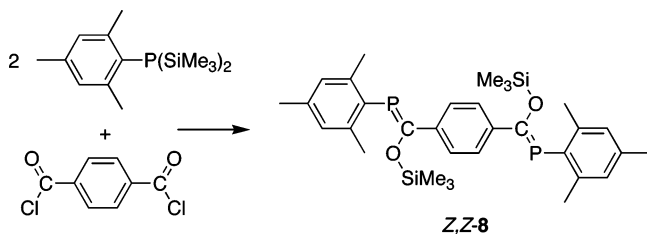


Figure 2. Molecular structure of *Z,Z*-**8** (50% probability). All hydrogen atoms are omitted for clarity.

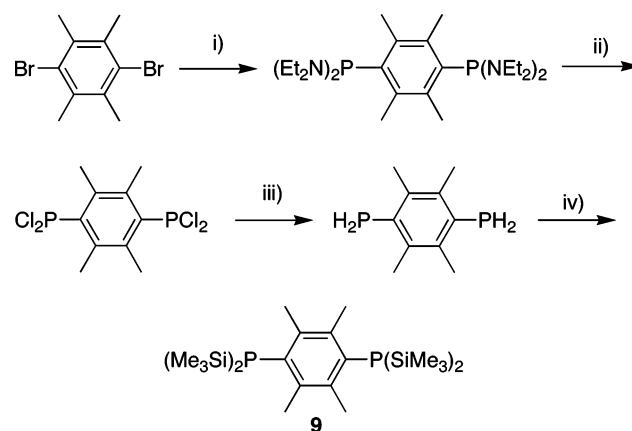
by X-ray crystallography confirmed that the *Z*-isomer was formed selectively (Figure 1).

In contrast to the conditions necessary for the preparation of bis(phosphaalkenes) *E/Z*-**5** and *E/Z*-**6** (several days of heating), bis(phosphaalkene) **8** forms quantitatively in just 5 h at 25 °C. The ³¹P NMR spectrum of the reaction mixture shows a single resonance at 146.3 ppm suggesting a single isomer. Crystals of bis(phosphaalkene) **8** suitable for X-ray crystallography were obtained directly from the reaction mixture, and the molecular structure (Figure 2) confirms the identity of **8** as a *Z,Z*-isomer.



To access bis(phosphaalkene) (**10**) and **PPP** (**11**) and fully test our hypothesis that bulky P-substituents preferentially give *Z*-phosphaalkenes, the hindered bis(phosphino)arylene (**9**) had to be prepared. Highly pyrophoric **9** was prepared following the procedure outlined in Scheme 2 (overall yield = 20%). Silylphosphine **9** is extremely difficult to obtain in high purity because of incomplete lithiation of 1,4-Br₂C₆Me₄ and the unavoidable presence of traces of [HNEt₃]Cl in the CIP(NEt₂)₂. Consequently, the first step yields some HC₆Me₄P(NEt)₂ and BrC₆Me₄P(NEt)₂ in addition to desired 1,4-C₆Me₄[P(NEt)₂]₂. We have found that when these impurities are removed by

Scheme 2^a



^a Conditions and reagents: (i) THF, −78 °C, 4 equiv ^tBuLi; subsequently, 2 equiv of CIP(NEt)₂. (ii) CH₂Cl₂, 0 °C, excess dry HCl(g). (iii) Et₂O, −78 °C, 1.1 equiv of LiAlH₄. (iv) Et₂O, −78 °C, 4 equiv of MeLi; subsequently, 4 equiv of ClSiMe₃.

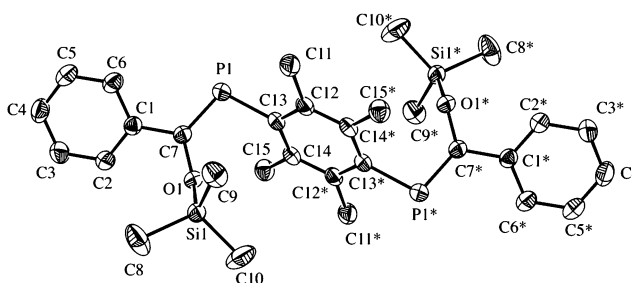
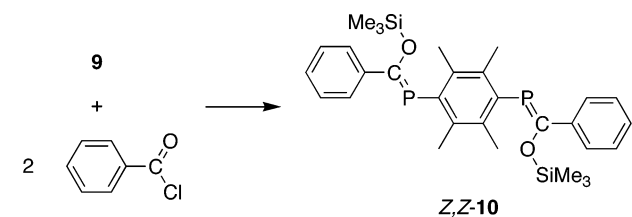


Figure 3. Molecular structure of *Z,Z*-**10** (50% probability). All hydrogen atoms are omitted for clarity.

careful fractional sublimation at the dichlorophosphine stage [i.e., from 1,4-C₆Me₄(PCl₂)₂], silylphosphine **9** can be isolated in very high purity.

With bis(silylphosphine) **9** in hand, the bis(phosphaalkene) (**10**) is obtained quantitatively by ³¹P NMR spectroscopy and in 62% isolated yield after recrystallization. Analogous to *Z*-**7** and *Z,Z*-**8**, the resonances assigned to the P=C bond in the ³¹P and ¹³C{¹H} NMR spectra of **10** (δ_{31P} = 150.2; δ_{13C} = 195.9, ¹J_{PC} = 55 Hz) suggest that a single *Z,Z*-isomer is obtained.⁴⁹ The selective formation of *Z,Z*-**10** is confirmed by the X-ray crystal structure (Figure 3).

The synthesis of the corresponding all *trans*-isomer **PPP** (**11**) was attempted by heating neat **9** and terephthaloyl chloride to 85 °C. After just 2 h, the initially free-flowing melt solidifies into a bright orange glass. The brittle solid, presumed to be **Z**-**11**, is insoluble in common organic solvents which is not surprising since many stereoregular organic π-conjugated polymers are poorly soluble (e.g., *trans*-PPV and *trans*-

(49) In addition to the large signal assigned to the *Z,Z*-isomer, the ³¹P NMR spectrum of the initial reaction mixture showed additional minor signals in the region expected for phosphaalkenes. This may indicate that a very small amount of *E*-isomer is present initially.

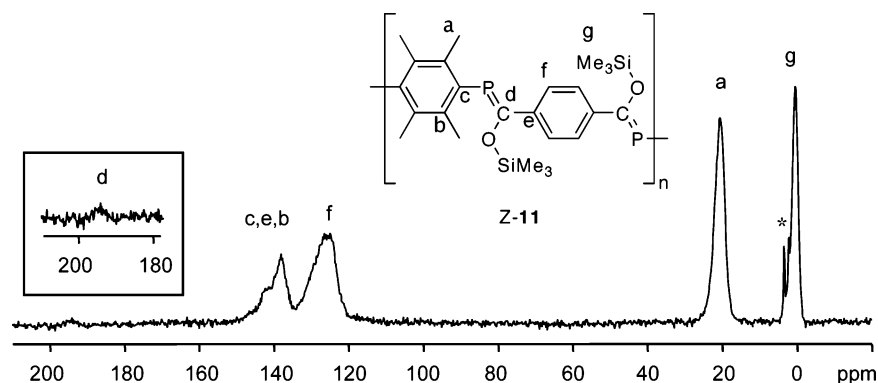
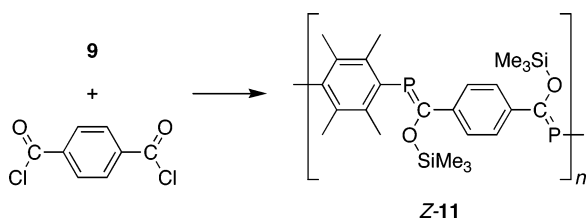


Figure 4. $^{13}\text{C}\{^1\text{H}\}$ CP-MAS NMR spectrum ($\nu_0 = 15$ kHz) of polymer **11** (10 000 scans, 5 s delay, contact time 1 s). * represents tentatively assigned to $-\text{P}(\text{SiMe}_3)_2$ end groups in **11** and/or unreacted **9**.

polyacetylene).⁵⁰ Solid-state NMR spectroscopy confirms that the orange glass is indeed **Z-11**. In particular, the dominant signal detected at 153 ppm in the ^{31}P CP-MAS NMR spectrum of **11** is assigned to the *Z*-phosphaalkene group upon comparison with **Z-7** ($\delta = 141.5$), **Z,Z-8** ($\delta = 146.3$), and **Z,Z-10** ($\delta = 150.2$). Signals at -147 and -155 ppm are assigned to $-\text{P}(\text{SiMe}_2)_2$ end groups and residual **9**, respectively. A small signal is also observed at δ 30 in the ^{31}P CP-MAS NMR spectrum. We speculate that either a bis(acyl)phosphine cross-link/branch point or a 1,2- or 1,3-diphosphetane cross-link is responsible for this signal since both moieties are plausible and are expected to resonate in this region of the ^{31}P NMR spectrum. Given that we have not observed $\text{P}=\text{C}$ dimerization in any of our model studies, we favor the assignment of the resonance at 30 ppm to the bis(acyl)phosphine. Moreover, we have prepared $\text{MesP}(\text{C}(\text{O})\text{Ph})_2$ ($\delta_{^{31}\text{P}} = 24.9$) as a model for the cross-link/branch points, and its ^{31}P chemical shift is similar to that observed in the solid-state NMR spectrum of **Z-11**.



Additional support for our assertion that polymer **11** is primarily *Z*-configured is provided by the $^{13}\text{C}\{^1\text{H}\}$ CP MAS solid-state NMR spectrum (Figure 4). The signal observed at 194 ppm is typical of the chemical shifts of vinylene carbon of $\text{Z-P}=\text{C}$ moieties in the model compounds as the *E-P}=\text{C} moieties are all observed further downfield at ca. 210 ppm (see Table 1). The other signals in the aryl and alkyl regions of the $^{13}\text{C}\{^1\text{H}\}$ CP MAS NMR spectrum are also consistent with the assigned structure of **Z-11**.*

It is possible that the partial cross-linking/branching of **11** observed in the thermal polymerization is due to slight stoichiometric imbalances in the melt [i.e., localized excess of $-\text{C}(\text{O})\text{Cl}$ moieties with respect to $-\text{P}(\text{SiMe}_3)_2$]. We speculated that better monomer mixing in a solution polymerization might minimize the formation of bis(acyl)phosphine cross-links/branches. Treating a THF solution of silylphosphine **9** with 1,4- $\text{C}_6\text{H}_4(\text{COCl})_2$ and monitoring the reaction progress by ^{31}P NMR

spectroscopy (Figure 5) gave some very intriguing results. As expected, over the course of 8 h silylphosphine **9** is entirely consumed and only a trace of bis(acyl)phosphine is observed ($\delta = 30$). Surprisingly, early in the reaction (i.e., Figure 5a and 5b), the majority of the phosphaalkene signals are observed at 175 ppm. This is significantly downfield from model compounds **Z-7**, **Z-8**, **Z-10**, and thermal polymer **Z-11** ($\delta = \text{ca. } 150$) and suggests *E*-isomer formation. As the polymerization progresses, the *E-P}=\text{C} moieties ($\delta = 175$) are consumed and the *Z-P}=\text{C} signals ($\delta = 150$) become dominant. The detection of *E*- before *Z*-isomers in Becker reactions has been mentioned previously^{45,51} and implies that the *Z*-phosphaalkene is formed from the *E*-phosphaalkene. In addition, it suggests that [1,3]-silylropy to form Becker phosphaalkenes is an intramolecular reaction since the acylphosphine can only adopt the conformation necessary to form an *E*- (but not *Z*-) phosphaalkene. If the silylropic rearrangement was intermolecular, there would be no preference for initial formation of the *E*- over the *Z*-isomer. Interestingly, after several hours an insoluble orange/brown solid precipitates from the reaction mixture (presumably, high molecular weight **Z-11**). The THF soluble portion of this precipitate of **11** was analyzed by UV/vis spectroscopy ($\lambda_{\text{max}} = 394$ nm).**

π -Conjugation in PPPs. In this section, the π -conjugation in poly(*p*-phenylenephosphaalkenes) will be assessed by examining the molecular structures of model compounds for the polymer and by using UV/vis spectroscopy. This section aims to show that there is strong evidence of π -conjugation between the $\text{P}=\text{C}$ and phenylene groups in these novel molecules and polymers.

(i) Structural Studies Using X-ray Crystallography. A coplanar relationship between the vinylene and phenylene groups in the **PPV** backbone would maximize the overlap of neighboring *p*-orbitals and, therefore, maximize π -conjugation. However, in **PPV**, deviations from coplanarity are observed, and short model oligomers of **PPV** [i.e., $\text{PhHC}=\text{CHPh}$ and $\text{Ph}(\text{HC}=\text{CH}-\text{C}_6\text{H}_4)_n\text{HC}=\text{CH}-\text{Ph}$; $n = 3$] show dihedral angles between the arylene and vinylene moieties of 3° – 10° .⁵² To gain insight into the π -conjugation in **PPP**s and to further investigate their

(51) Yoshifuji, M.; Toyota, K.; Shibayama, K.; Inamoto, N. *Chem. Lett.* **1983**, 1653–1656.

(52) van Hutten, P. F.; Wildeman, J.; Meetsma, A.; Hadziioannou, G. *J. Am. Chem. Soc.* **1999**, *121*, 5910–5918. Kwasniewski, S. P.; François, J. P.; Deleuze, M. S. *J. Phys. Chem. A* **2003**, *107*, 5168–5180. Traetteberg, M.; Frantsen, E. B. *J. Mol. Struct.* **1975**, *26*, 57–68. Bernstein, J. *Acta Crystallogr.* **1975**, *B31*, 1268–1271. Hoekstra, A.; Meertens, P.; Vos, A. *Acta Crystallogr.* **1975**, *B31*, 2813–2817. Finder, C. J.; Newton, M. G.; Allinger, N. L. *Acta Crystallogr.* **1974**, *B30*, 411–415. Robertson, J. M.; Woodward, I. *Proc. R. Soc. London, Ser. A* **1937**, *162*, 568–570.

(50) Skotheim, T. A. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986; Vol. I and II.

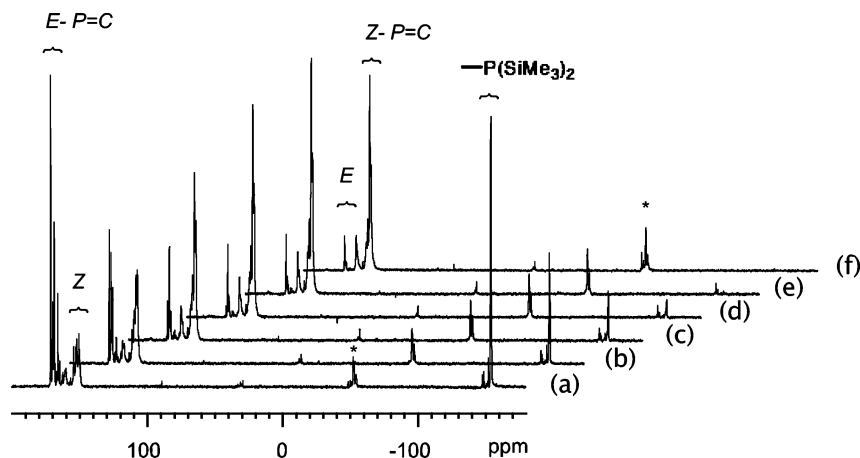


Figure 5. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra showing the progress of the reaction of **9** with 1,4- $\text{C}_6\text{H}_6(\text{COCl})_2$ in THF. Spectra collected after (a) 15 min, (b) 1 h, (c) 2 h, (d) 4 h, (e) 6 h, and (f) 8 h. * represents hydrolysis product.

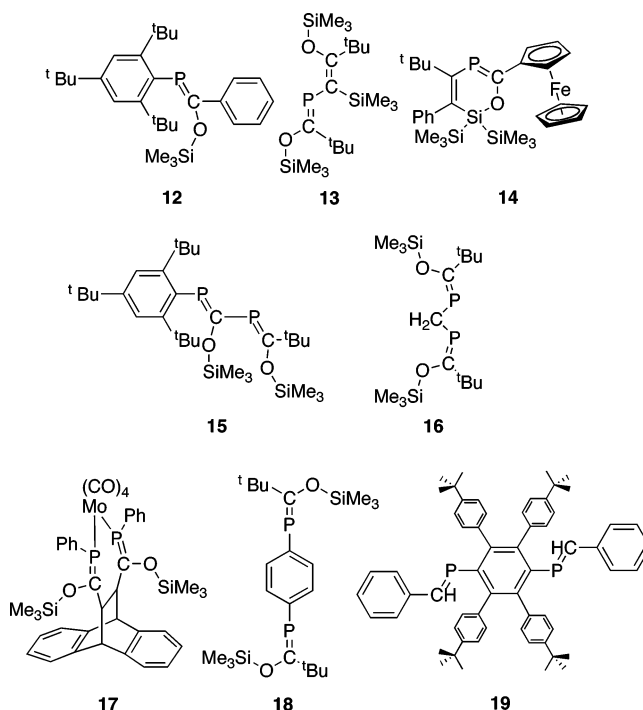
Table 2. Crystal Data and Structural Refinement Details for **7**, **8**, and **10**

	7	8	10
formula	$\text{C}_{19}\text{H}_{25}\text{OPSi}$	$\text{C}_{30}\text{H}_{40}\text{O}_2\text{P}_2\text{Si}_2$	$\text{C}_{32}\text{H}_{44}\text{O}_2\text{P}_2\text{Si}_2$
FW	328.45	550.74	578.82
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P1$
color	yellow	yellow	yellow
a (Å)	7.806(1)	9.769(1)	8.1006(7)
b (Å)	16.799(2)	9.0886(8)	12.280(1)
c (Å)	14.801(2)	17.490(2)	17.181(2)
α (deg)	90.0	90.0	101.513(5)
β (deg)	101.780(10)	94.19(1)	93.354(4)
γ (deg)	90.0	90.0	98.714(4)
V (Å ³)	1900.0(4)	1548.7(3)	1648.4(3)
Z	4	2	2
T (K)	173(2)	173(1)	173(1)
d_{calcd} (Mg m ⁻³)	1.148	1.181	1.166
crystal size (mm ³)	$0.50 \times 0.50 \times 0.10$	$0.30 \times 0.20 \times 0.10$	$0.35 \times 0.20 \times 0.10$
no. reflns	45 391	32 704	15 587
no. unique reflns	4456	3671	6806
R (int)	0.0330	0.032	0.055
reflection/params	4456/204	3671/168	6806/353
$R1$ [$I > 2\sigma(I)$] ^a	0.035	0.048	0.042
$wR2$ [all data] ^b	0.108	0.138	0.103
GOF	1.123	1.05	0.92

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)]^{1/2}.$$

structural features and bonding, the molecular structures of **Z-7**, **Z-8**, and **Z-10** (Figures 1, 2, and 3, respectively) were determined by X-ray crystallography. A summary of data collection and refinement parameters is listed in Table 2, and the bond lengths and angles for these and other phosphalkenes pertinent to this discussion are summarized in Table 3. A survey of the Cambridge Crystallographic Database (CCD) for possible molecular models for the **PPPs** reported herein revealed 22 Becker-type phosphalkenes.^{40b,48,53–65} Of these, just seven

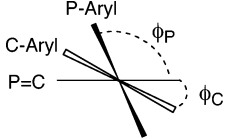
feature carbon substituents on both the phosphorus and carbon atoms of the P=C bond (**12**,⁴⁸ **13**,⁵³ **14**,⁵⁴ **15**,⁵⁵ **16**,^{40b} **17**,⁵⁶ and **18**⁵⁷). To our knowledge, two other 1,4-arylene-bridged bis-(phosphaalkene)s have previously been crystallographically characterized (**18**⁵⁷ and **19**⁶⁶).



The P=C bonds in model compounds **7**, **8**, and **10** are comparable in length [avg 1.701(4) Å] and are similar to those found in the Becker phosphalkenes **12–18** [avg 1.690(6) Å]. This places these molecules near the upper limit of a typical P=C bond length [1.61–1.71 Å].³⁵ The bond angles at phosphorus for **7**, **8**, and **10** (avg 104°) are consistent with a high degree of p-character for the P–C σ -bonds and a high

- (53) Manz, B.; Bergstasser, U.; Kerth, J.; Maas, G. *Chem. Ber.* **1997**, *130*, 779–788.
 (54) Haber, S.; Schmitz, M.; Bergstasser, U.; Hoffman, J.; Regitz, M. *Chem.—Eur. J.* **1999**, *5*, 1581–1589.
 (55) Appel, R.; Fölling, P.; Schuhn, W.; Knoch, F. *Tetrahedron Lett.* **1986**, *27*, 1661–1664.
 (56) Appel, R.; Hunnerbein, J.; Knoch, F.; Nieger, M. *J. Organomet. Chem.* **1988**, *346*, 379–384.
 (57) Knoch, F.; Appel, R.; Wenzel, H. Z. *Krystallogr.* **1995**, *210*, 224–224.
 (58) Appel, R.; Barth, V.; Knoch, F. *Chem. Ber.* **1983**, *116*, 938–950.
 (59) Weber, L.; Reizig, K.; Boese, R.; Polk, M. *Angew. Chem., Int. Ed.* **1985**, *24*, 604–605.
 (60) Weber, L.; Reizig, K.; Frebel, M.; Boese, R.; Polk, M. *J. Organomet. Chem.* **1986**, *306*, 105–114.
 (61) Weber, L.; Reizig, K.; Boese, R.; Polk, M. *Organometallics* **1986**, *5*, 1098–1103.
 (62) Appel, R.; Porz, C.; Knoch, F. *Chem. Ber.* **1986**, *119*, 2748–2755.

- (63) Appel, R.; Niemann, B.; Schuhn, W.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 932–932.
 (64) Appel, R.; Fölling, P.; Josten, B.; Schuhn, W.; Wenzel, H. V.; Knoch, F. *Z. Anorg. Allg. Chem.* **1988**, *556*, 7–22.
 (65) Grünhagen, A.; Pieper, U.; Kottke, T.; Roesky, H. W. *Z. Anorg. Allg. Chem.* **1994**, *620*, 716–722.
 (66) Shah, S.; Concolino, T.; Rheingold, A. L.; Protasiewicz, J. D. *Inorg. Chem.* **2000**, *39*, 3860–3867.

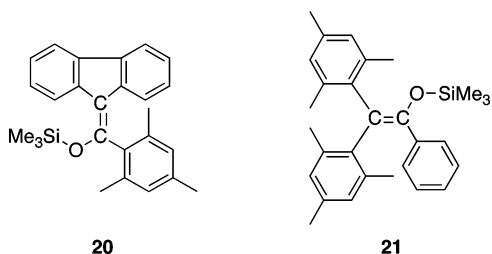
Table 3. Comparison of Important Structural Data


compd	P=C bond [Å]	angle between planes [deg]		C–P=C angle [deg]	CP=CC torsion angle [deg]	reference
		ϕ_P^b	ϕ_C^c			
7	1.7081(12)	65.6(2)	27.8(2)	104.20(6)	178.1(1)	this work
8^a (P1)	1.700(2)	62.18(2)	16.5(2)	106.31(9)	179.1(1)	this work
(P2)	1.696(2)	66.67(2)	26.55(2)	104.19(9)	–176.2(1)	this work
10	1.7014(19)	59.88(8)	25.54(9)	102.94(9)	179.9(1)	this work
12	1.686(2)	81.6(3)	54.8(2)	103.9(2)	–175.2(1)	48
18	1.683(2)	56.8(2)	N/A ^d	104.6(2)	–174.6(1)	57
19	1.676(2)	69.9(2)	21.8(2)	101.4(2)	172.07(2)	66

^a The P=C units are unique in **8**. ^b This is the angle between the planes defined by the 6-atom P-substituted aromatic ring and the 5-atom plane containing the P=C bond, calculated using ConQuest. ^c This is the angle between the planes defined by the 6-atom C-substituted aromatic ring and the 5-atom plane containing the P=C bond, calculated by ConQuest. ^d Due to the alkyl substituent on the carbon atom, ϕ_C cannot be defined.

degree of s-character for the lone pair. The sum of the bond angles at the P=C carbon and the C–P=C–C torsion angles in **7**, **8**, and **10** are as expected for a planar double bonded system and do not deviate significantly from 360° and 180°, respectively.

The angles between the planes of the P=C bond and the aryl substituents are most relevant to the structural assessment of the π -conjugation in phosphoranes **7**, **8**, and **10** in the solid state. The degree of π -conjugation is proportional to the cosine of the angle (ϕ) between planes (i.e., $\phi = 90^\circ \rightarrow$ no π -conjugation). The dihedral angles between the P=C plane and the bulky aryl P-substituent for each of the model compounds [**7** $\phi_P = 65.6(2)^\circ$; **8** $\phi_P = 62.18(2)^\circ$, $66.67(2)^\circ$; **10** $\phi_P = 59.88(8)^\circ$] does not preclude π -conjugation between these moieties but will prevent efficient delocalization of the pi-system. For comparison, stilbene derivatives with a Mes substituent (i.e., **20**, $\phi_{\text{Mes}} = 76^\circ$; **21**, $\phi_{\text{Mes}} = 62^\circ$) exhibit similar dihedral angles and are much larger than those found in *trans*-stilbene ($\phi_{\text{Ph}} = 3^\circ$ – 10°). Other *trans*-aryl substituted phosphoranes also show significant twist angles for the P-substituents [Z-**12**: $\phi_P = 81.6(2)^\circ$; Z,Z-**18**: $\phi_P = 56.8(2)^\circ$; E,E-**19**: $\phi_P = 69.9(2)^\circ$], but only Z-**12**, possessing the extremely bulky Mes* group, approaches 90° (i.e., no π -conjugation).



The angles between the planes of the P=C bond and the sterically unhindered C-substituent [**7** $\phi_C = 27.8(2)^\circ$; **8** $\phi_C = 16.5(2)^\circ$, $26.55(2)^\circ$; **10** $\phi_C = 25.54(9)^\circ$] are much smaller enabling greater π -conjugation between these moieties. For

(67) Brook, A. G.; Chatterton, W. J.; Sawyer, J. F.; Hughes, D. W.; Vorspohl, K. *Organometallics* **1987**, *6*, 1246–1256.

(68) Schmittel, M.; Keller, M.; Burghart, A. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2327–2333.

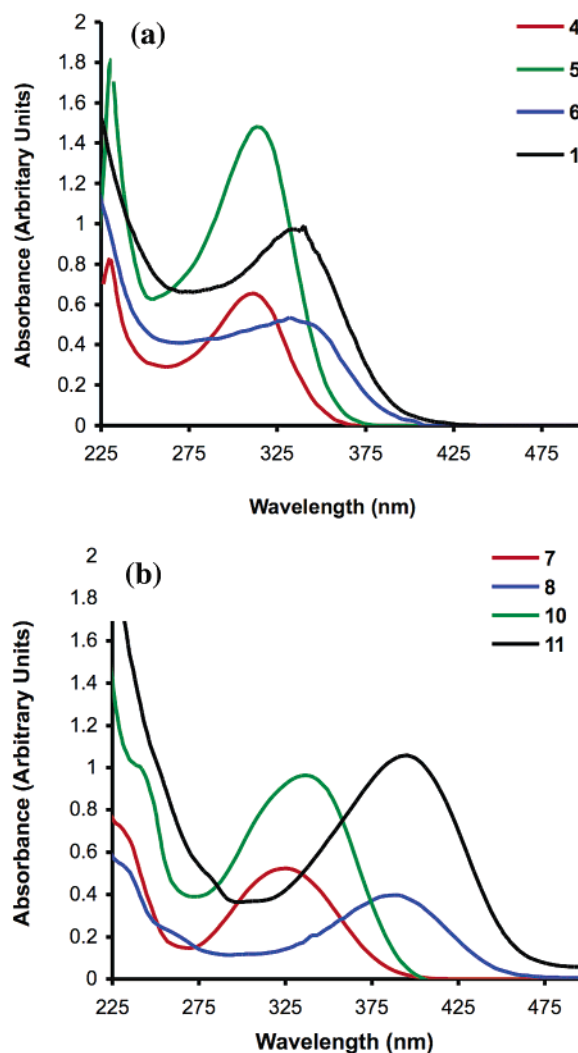


Figure 6. UV/vis spectra (ca. 10^{-5} M THF) of (a) *E/Z*-model compounds (**4**, **5**, **6**) and PPP (**1**) and (b) all *Z*-model compounds (**7**, **8**, and **10**) and the THF soluble portion of PPP (**11**).

comparison, the structurally related mono(phosphorane) Z-**12** [$\phi_C = 54.8(2)^\circ$] shows a much larger angle and is less π -conjugated. The bis(phosphorane) *E,E*-**19** [$\phi_C = 21.8^\circ$] exhibits a small twist angle that is comparable to the ϕ_C for **7**, **8**, and **10** and suggests a similar degree of π -conjugation.

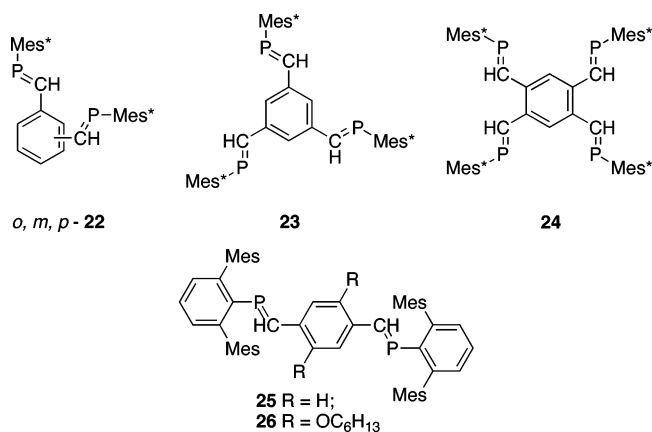
In conclusion, the observed angles between the P=C and arylene planes in model phosphoranes Z-**7**, Z,Z-**8**, and Z,Z-**10** suggest that PPP will show properties consistent with π -conjugation. Unfortunately, it is not possible to ascertain to what extent the structural features are determined by electronics (i.e., conjugation effects) versus crystal packing effects. In solution, it may be possible to access more conjugated planar structures at least in excited states.

(ii) Electronic Properties Using UV/Vis Spectroscopy. For extended π -conjugated systems, a red shift in λ_{max} of the π – π^* band is observed as the length of the conjugation pathway is increased.^{69,70} Therefore, if the P=C bond and arylene unit are π -conjugated, the λ_{max} should increase from mono(phosphorane)s to bis(phosphorane)s to the corresponding PPP. Previous studies of a series of model compounds of PPP (**2**)

(69) Meier, H.; Stalmach, U.; Kolshorn, H. *Acta Polym.* **1997**, *48*, 379–384.

(70) Müllen, K.; Wegner, G., Eds. *Electronic Materials. The Oligomer Approach*; Wiley-VCH: New York, 1998.

by Smith and Protasiewicz⁴¹ and investigations of *ortho*, *meta*, and *para*-**22**,^{71–74} **23**, and **24**^{75,76} have provided strong evidence that phosphalkenes are capable of long-range electronic communication in π -systems. The UV/vis spectra for the phosphalkenes prepared in this study are shown in Figure 6, and the λ_{\max} data are tabulated in Table 1. A red shift is observed in the absorbance maximum assigned to the π - π^* band as the chain length is increased for the *E/Z*-phosphalkenes [**4**, 310 nm; **5**, 314 nm; **6**, 332 nm; **1**, 338 nm] and the *Z*-phosphalkenes [**7**, 324; **8**, 388 nm; **10**, 337 nm; **11**, 394 nm]. For comparison, the λ_{\max} for *Z*-**11** (394 nm) is less than that for *E*-**PPV** (426 nm)⁷⁷ and **PPP** (*E*-**2**, 445 nm).³⁹ Importantly, the magnitude of the red shift is greater for the all *Z*-**PPP** ($\Delta\lambda_{\max} = 70$ nm for **11** vs **7**) than for the mixed *E/Z*-**PPP** ($\Delta\lambda_{\max} = 28$ nm for **1** vs **4**) and *E*-**2** ($\Delta\lambda_{\max} = 0$ nm vs **26**). Interestingly, the red shifts observed for known **PPP**s are smaller than the red shift for *E*-**PPV** ($\Delta\lambda_{\max} = 119$ nm vs *E*-stilbene). The smaller red shift for **PPP**s is likely a consequence of twisting in the backbone caused by the C_6Me_4 moieties. The incorporation of some C_6Me_4 groups into **PPV** is known to lead to a blue shift of 20–30 nm.^{77,78}



Although the C_6Me_4 group partially impedes π -conjugation, the modest red shifts observed between the bis- and mono-(phosphalkene)s ($\Delta\lambda_{\max} = 4$ nm for **5** vs **4**; $\Delta\lambda_{\max} = 13$ nm for **10** vs **7**) suggest that there is still π -conjugation through the central C_6Me_4 ring in **PPP**s. If the $P=C$ bonds were

electronically isolated no significant bathochromic shift in the λ_{\max} for these pairs of compounds would be expected. Nevertheless, the longer wavelength absorbances observed for bis-(phosphalkene)s with C_6H_4 -spacers over those with C_6Me_4 -spacers ($\Delta\lambda_{\max} = 18$ nm for **6** vs **5**; $\Delta\lambda_{\max} = 51$ nm **8** vs **10**) suggest more effective π -conjugation through the less sterically bulky spacer. A similar observation was also made with bis-(phosphalkene)s **25** and **19**.^{41,79} In preliminary luminescence measurements a weak emission is detected at 445 nm when THF solutions of polymer **1** are excited at 310 nm.

Summary

We have synthesized a new class of π -conjugated polymer, poly(*p*-phenylenephosphalkene) (**PPP**), a phosphorus copy of poly(*p*-phenylenevinylene) (**PPV**). The formal replacement of $C=C$ bonds by the isolobal $P=C$ bonds extends the phosphorus–carbon analogy to polymer science. Importantly, we have discovered that the positioning of the bulky substituent required to kinetically stabilize the $P=C$ bond provides a measure of stereochemical control. The more highly conjugated *Z*-isomer, which features the aryl substituents in a *trans* arrangement to one another, is formed selectively when the *ortho*-dimethyl-substituted arene is placed on phosphorus while *E/Z*-mixtures are observed otherwise. Strong evidence for π -conjugation between the $P=C$ and phenylene groups in **PPP**s has been gathered from UV/vis spectroscopy and X-ray crystallography on molecular model compounds. Specifically, the molecular structures obtained for mono- and bis(phosphalkene)s show small twist angles between the $P=C$ plane and unsubstituted arenes (16° – 26°) and larger twist angles between the $P=C$ plane and methyl-substituted arenes (59° – 67°). A remarkable 70 nm red shift is observed for a THF soluble fraction of *Z*-**PPP** when compared with a mono(phosphalkene) model compound. Future work will focus on preparing soluble *Z*-**PPP**s and gaining further insight into the electronic properties of this new class of phosphorus macromolecule.

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Supporting Information Available: Details of X-ray structure determinations as .cif files, detailed experimental procedures, and spectroscopic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (71) Jouaiti, A.; Geoffroy, M.; Bernardinelli, G. *Chem. Commun.* **1996**, 437–438.
 (72) Jouaiti, A.; Geoffroy, M.; Terron, G.; Bernardinelli, G. *J. Chem. Soc., Chem. Commun.* **1992**, 155–156.
 (73) Jouaiti, A.; Geoffroy, M.; Terron, G.; Bernardinelli, G. *J. Am. Chem. Soc.* **1995**, *117*, 2251–2258.
 (74) Badri, A.; Jouaiti, A.; Geoffroy, M. *Magn. Reson. Chem.* **1999**, *37*, 735–742.
 (75) Kawanami, H.; Toyota, K.; Yoshifuji, M. *Chem. Lett.* **1996**, 533–534.
 (76) Kawanami, H.; Toyota, K.; Yoshifuji, M. *J. Organomet. Chem.* **1997**, *535*, 1–5.
 (77) Simmons, W. W. *The Sadtler Handbook of Ultraviolet Spectra*; Sadtler Research Laboratories: Philadelphia, PA, 1979.
 (78) Chung, S.; Lee, D. W.; Oh, D. K.; Lee, C. E.; Jin, J. *Acta Polym.* **1999**, *50*, 298–303.

- (79) Smith, R. C.; Urnezus, E.; Lam, K.-C.; Rheingold, A. L.; Protasiewicz, J. D. *Inorg. Chem.* **2002**, *41*, 5296–5299.