Inorg. Chem. **2006**, *45*, 4895–4901

Inorganic Chemistry
Article

Photochemical *E*–*Z* Isomerization of *meta*-Terphenyl-Protected Phosphaalkenes and Structural Characterizations

Vittal B. Gudimetla,[†] Arnold L. Rheingold,[‡] John L. Payton,[†] Huo-Lei Peng,[†] M. Cather Simpson,[†] and John D. Protasiewicz*,[†]

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106-7708, and Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, California 92093

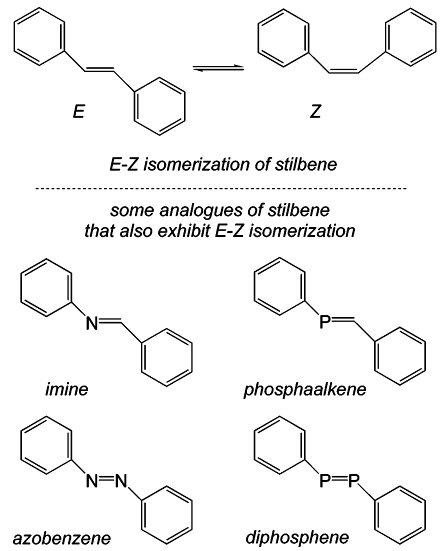
Received November 29, 2005

A series of phosphaalkenes, *E*-ArP═C(H)Ar′ (Ar = 2,6-$Mes_2C_6H_3$, Ar′ = Ph (**1a**); Ar = 2,6-$Mes_2C_6H_3$, Ar′ = *p*-C_6H_4Br (**2a**); Ar = 4-Br-2,6-$Mes_2C_6H_2$, Ar′ = Ph (**3a**); Ar = 4-Br-2,6-$Mes_2C_6H_2$, Ar′ = *p*-C_6H_4Br (**4a**)) have been prepared by phospha-Wittig reactions and characterized. Exposure of these materials either to room light over an extended period of time (days) or to UV light (hours) produced equilibrium mixtures of the *E* and *Z* isomers (**1b**–**4b**) as indicated by ^1H and ^{31}P NMR spectroscopy. The structures of compounds **4a** and **4b** were determined by single-crystal X-ray diffraction methods. Variable-temperature ^1H NMR studies of **4b** indicate hindered rotation about the P–C^{Ar} bond, with $\Delta H^{\ddagger} = 13.8$ kcal/mol and $\Delta S^{\ddagger} = 1.3$ eu. The electronic structures of *E*- and *Z*-PhP═C(H)Ph have been examined using density functional theory.

Introduction

The photochemically promoted *E* to *Z* isomerizations of olefins are a very important class of reactions for chemical and biological processes.[1] Stilbenes (Ar(H)C═C(H)Ar) and stilbenoid compounds are perhaps the most well-studied materials for this important fundamental aspect of photochemistry (Chart 1). Applications involving stilbenoid-based materials and light include molecular switches, organic light-emitting diodes (OLEDs), nonlinear optics, photovoltaics, laser dyes, etc.[2] Likewise, isomerization reactions of both imines (Ar_2C═NAr) and azobenzenes (ArN═NAr) have attracted considerable attention for various applications as photoresponsive materials.[3]

Chart 1



Analogous isomerization reactions of compounds featuring main group element multiple bonds are far less frequently studied because of the higher reactivity of such materials compared to their carbon-based analogues and the resultant greater steric bulk required for their isolation.[4] Organophosphorus compounds have received a great deal of attention within this field because of their parallel relationship with well-established carbon compounds and chemistry.[5] In particular, phosphorus analogues of stilbene, such as the phosphaalkene Mes*P═C(H)Ph[6] (**A**) and the diphosphene

---

* To whom correspondence should be addressed. E-mail: protasiewicz@case.edu.

[†] Case Western Reserve University.

[‡] University of California San Diego.

(1) For reviews, see: (a) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415. (b) Momotake, A.; Arai, T. *J. Photochem. Photobiol. C* **2004**, *5*, 1.

(2) Meier, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1399−1540.

(3) (a) Horspool, W.; Lenci, F. *CRC Handbook of Organic Photochemistry and Photobiology*, 2nd ed.; CRC Press: Boca Raton, FL, 2004. (b) Wettermark, G. *Chemistry of the Carbon−Nitrogen Double Bond*; Patai, S., Ed.; Interscience Publishers: London, 1970; p 565.

(4) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463.

10.1021/ic0520521 CCC: $33.50

Mes*P=PMes*[7] (**B**) (Mes* = 2,4,6-$^{t}Bu_3C_6H_2$) have been shown to yield mixtures of *E* and *Z* isomers upon irradiation. Related compounds having two or more Mes*P=C(H) functional groups display similar light-induced isomerization.[8]

Lately these phosphaalkene group-containing materials have also shown great promise as ligands for transition metal complexes and, in some cases, can be used in a number of important catalytic reactions.[9] The orientation of the substituents about the P=C bond dictate the coordination mode and catalytic efficacy of such ligands.

Interestingly, we and others have noted the absence of photoisomerization of meta-terphenyl diphosphenes ArP=PAr (Ar = 4-Me-2,6-$Mes_2C_6H_2$)[10] and DmpP=PDmp (Dmp = 2,6-$Mes_2C_6H_3$)[11] upon irradiation. This apparent lack of photoactivity is in contrast with the rich photochemistry observed for the Mes*P=PMes* diphosphene. This result presumably reflects the differences in the overall shape of the two types of sterically demanding groups. No photochemical studies have been reported for phosphaalkenes bearing *meta*-terphenyl groups, and thus it would be of interest to determine if this dichotomy extends to the corresponding *meta*-terphenyl-protected phosphaalkenes.

Recently, we initiated efforts to systematically synthesize a series of phosphaalkenes of the form *E*-ArP=C(H)Ar′ (Ar = 4-X-2,6-$Mes_2C_6H_2$, Ar′ = 4-Y−C_6H_4) where the presence of the X and Y groups would allow the elimination of XY equivalents via catalytic coupling reactions. Such an approach facilitates the construction of new materials with nonlinear optical properties and the synthesis of new conjugated polymers with low-coordinate phosphorus atoms.[12,13] During these efforts, we noted that extended handling of these phosphaalkenes in room light produced the corresponding *Z* isomers. Herein we present a report on the photochemical isomerization of a previously reported phosphaalkene and three new bromine-substituted derivatives.

Experimental Section

General Procedures. All manipulations were carried out using modified Schlenk techniques or in a MBraun Labmaster 130 drybox under N_2. Solvents were purified by distillation from Na-benzophenone ketyl under a N_2 atmosphere before use. $DmpPCl_2$,[14] DmpP=C(H)Ph (**1a**),[15] and 4-Br-2,6-$Mes_2C_6H_2I$[16] were prepared as previously described. UV−vis absorption spectra were recorded using a Cary500 spectrophotometer. All photochemical reactions were performed in $CDCl_3$ at room temperature in a Rayonet photochemical reactor loaded with 350 nm UV source lamps. Routine NMR data were recorded on a Varian Inova spectrometer operating at 400 MHz and 161.8 MHz for the ^{1}H and ^{31}P spectra, respectively. ^{31}P NMR data are referenced to external 85% H_3PO_4, while the ^{1}H NMR data are referenced to residual proton solvent signals of $CDCl_3$. VT NMR studies were performed using a 600 MHz Varian Inova NMR instrument.

4-Br-2,6-$Mes_2C_6H_2PCl_2$. In a 100 mL dry round-bottom flask, a solution of 2.00 g of 4-Br-2,6-$Mes_2C_6H_2I$ (3.85 mmol) dissolved in 20 mL of THF was chilled to −78 °C; 1.77 mL of 2.5 M solution of *n*BuLi in hexanes (4.43 mmol) was added to this solution. Then the mixture was allowed to stir at −78 °C. After 2 h, 1.68 mL of PCl_3 (19.3 mmol) was added rapidly, and the reaction mixture was then allowed to warm to room temperature. The solvent was removed under vacuum, and the crude product was placed into a drybox where it was slurried in 30 mL of acetonitrile; then the mixture was filtered, and the product was washed with 5 mL of hexanes. The solid was dried under vacuum and then dissolved in diethyl ether; then the solution was filtered through Celite. The solvent was removed under vacuum, and the solid was then recrystallized from ether at −35 °C to yield 0.610 g of 4-Br-2,6-$Mes_2C_6H_2PCl_2$ (32%). ^{1}H NMR ($CDCl_3$): δ 7.29 (d, 2H, J_{PH} = 2.4 Hz), 6.91 (d, 4H, J_{HH} = 0.8 Hz), 2.32 (s, 6H), 2.03 (s, 12H). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 159.0. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 148.5, 148.2, 138.2, 136.4, 134.7, 133.4, 128.1, 127.8, 21.4, 21.2. mp: 200−202 °C. Anal. Calcd for $C_{24}H_{24}PBrCl_2$: C, 58.53; H, 4.92. Found: C, 58.36; H, 4.70.

---

(5) (a) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; John Wiley & Sons: New York, 1998. (b) *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M.; Scherer, O. J., Eds.; Thieme Verlag: Stuttgart, Germany, 1990.

(6) (a) Yoshifuji, M.; Toyota, K.; Inamoto, N. *Tetrahedron Lett.* **1985**, *26*, 1727. (b) Yoshifuji, M.; Toyota, K.; Inamoto, N. *Tetrahedron Lett.* **1985**, *26*, 6443. (c) Yoshifuji, M.; Toyota, K.; Matsuda, I.; Niitsu, T.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *Tetrahedron* **1988**, *44*, 1363. (d) Appel, R.; Menzel, J.; Knoch, F.; Volz, P. *Z. Anorg. Allg. Chem.* **1986**, *534*, 100.

(7) (a) Yoshifuji, M.; Sato, T.; Inamoto, N. *Chem. Lett.* **1988**, 1735. For some other examples of diphosphene photochemistry, see: (b) Weber, L. *Chem. Rev.* **1992**, *92*, 1839. (c) Yoshifuji, M.; Sato, T.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2394. (d) Jutzi, P.; Meyer, U. *J. Organomet. Chem.* **1987**, *333*, C18. (e)Yoshifuji, M.; Abe, M.; Toyota, K.; Goto, K.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1572. (f) Komen, C. M. D.; Kanter, F. J. J. d.; Goede, S. J.; Bickelhaupt, F. *J. Chem. Soc., Perkin Trans. 2* **1993**, 807. (g) Yoshifuji, M.; Abe, M.; Toyota, K.; Goto, K.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1572.

(8) (a) Jouaiti, A.; Geoffroy, M.; Terron, G.; Bernardinelli, G. *J. Am. Chem. Soc.* **1995**, *117*, 2251. (b) Kawanami, H.; Toyota, K.; Yoshifuji, M. *J. Organomet. Chem.* **1997**, *535*, 1.

(9) (a) Gajare, A. S.; Jensen, R. S.; Toyota, K.; Yoshifuji, M.; Ozawa, F. *Synlett* **2005**, 144. (b) Boubekeur, L.; Ricard, L.; Le Floch, P.; Mezailles, N. *Organometallics* **2005**, *24*, 3856. (c) Gajare, A. S.; Toyota, K.; Yoshifuji, M.; Ozawa, F. *J. Chem. Soc., Chem. Commun.* **2004**, 1994. (d) Grobe, J.; Le Van, D. *J. Fluorine Chem.* **2004**, *125*, 801. (e) Boettcher, H.-C.; Himmel, D.; Scheer, M. *Organometallics* **2004**, *23*, 5314. (f) Weber, L.; Lassahn, U.; Stammler, H.-G.; Neumann, B.; Karaghiosoff, K. *Eur. J. Inorg. Chem.* **2002**, 3272. (g) Weber, L.; Meyer, M.; Stammler, H.-G.; Neumann, B. *Chem.*−*Eur. J.* **2001**, *7*, 5401. (h) Weber, L.; Scheffer, M. H.; Stammler, H.-G.; Stammler, A. *Eur. J. Inorg. Chem.* **1999**, 1607. (i) van der Sluis, M.; Beverwijk, V.; Termaten, A.; Bickelhaupt, F.; Kooijman, H.; Spek, A. L. *Organometallics* **1999**, *18*, 1402. (j) Elschenbroich, C.; Voss, S.; Harms, K. *Z. Naturforsch., B: Chem. Sci.* **1999**, *54*, 209. (k) Weber, L.; Uthmann, S.; Boegge, H.; Mueller, A.; Stammler, H.-G.; Neumann, B. *Organometallics* **1998**, *17*, 3593. (l) Weber, L.; Quasdorff, B.; Stammler, H.-G.; Neumann, B. *Chem.*−*Eur. J.* **1998**, *4*, 469. (n) Bedford, R. B.; Hill, A. F.; Jones, C.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1998**, *17*, 4744. (o) Weber, L.; Kaminski, O.; Quasdorff, B.; Stammler, H.-G.; Neumann, B. *J. Organomet. Chem.* **1997**, *529*, 329. (p) van der Sluis, M.; Beverwijk, V.; Termaten, A.; Gavrilova, E.; Bickelhaupt, F.; Kooijman, H.; Veldman, N.; Spek, A. L. *Organometallics* **1997**, *16*, 1144. (q) Weber, L.; Kaminski, O.; Boese, R.; Blaeser, D. *Organometallics* **1995**, *14*, 820. (r) Jouaiti, A.; Geoffroy, M.; Terron, G.; Bernardinelli, G. *J. Am. Chem. Soc.* **1995**, *117*, 2251.

(10) Tsuji, K.; Sasaki, S.; Yoshifuji, M. *Heteroat. Chem.* **1998**, *9*, 607.

(11) Simpson, M. C.; Protasiewicz, J. D. Unpublished results.

(12) (a) Smith, R. C.; Chen, X.; Protasiewicz, J. D. *Inorg. Chem.* **2003**, *42*, 5468. (b) Smith, R. C.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **2004**, *126*, 2268.

(13) Wright, V. A. and Gates, D. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 2389.

(14) Urnezius, E.; Protasiewicz, J. D. *Main Group Chem.* **1996**, *1*, 369.

(15) Shah, S.; Protasiewicz, J. D. *J. Chem. Soc., Chem. Commun.* **1998**, 1585.

(16) (a) Tsuji, K.; Sasaki, S.; Yoshifuji, M. *Tetrahedron Lett.* **1999**, *40*, 3203. (b) Sasaki, S.; Aoki, H.; Sutoh, K.; Tsuji, K.; Yoshifuji, M. *Helv. Chim. Acta* **2002**, *85*, 3842.

***E*-[2,6-Mes$_2$C$_6$H$_3$P═C(H)C$_6$H$_4$Br] (2a).** A mixture of 0.10 g of DmpPCl$_2$ (0.24 mmol), 0.020 g of Zn dust (0.31 mmol), 0.050 g of *p*-bromobenzaldehyde (0.270 mmol), and 1.44 mL of a 1.00 M solution of PMe$_3$ in toluene (1.44 mmol) in 20 mL of THF was allowed to stir overnight in a 50 mL round-bottom flask. The reaction mixture was then filtered, and the solvent was removed under vacuum. The remaining solid was rinsed with acetonitrile and then extracted into hexanes. The product obtained after removal of the hexanes under vacuum was recrystallized from a concentrated ether solution at −35 °C to yield 0.060 g of yellow **2a** (50%). ^{1}H NMR (CDCl$_3$): δ 8.54 (d, 1H, $J_{PH} = 24.8$ Hz), 7.46 (t, $J_{HH} = 7.6$ Hz, 1H), 7.22 (d, $J_{HH} = 8.4$ Hz, 2H), 7.10 (d, $J_{HH} = 7.6$ Hz, 2H), 6.97 (m, 2H), 6.87 (s, 4H), 2.27(s, 6H), 2.05 (s, 12H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 178.2 (d, $J_{PC} = 35.1$ Hz), 140.6 (d, $J_{PC} = 39.0$ Hz), 144.8 (d, $J_{PC} = 3.0$ Hz), 139.0 (d, $J_{PC} = 14.5$ Hz), 138.2 (s), 137.1 (s), 135.6 (s), 131.4 (s), 129.6 (s), 128.6 (s), 128.2 (s), 127.2 (s), 121.8 (d, $J_{PC} = 8.0$ Hz), 21.1 (s), 20.9 (d, $J_{PC} = 2.0$ Hz) ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 245.7. UV−vis (CHCl$_3$): λ_{max} 342 nm, ($\epsilon = 12\,600$ M^{-1} cm^{-1}). mp: 132−134 °C. Anal. Calcd for C$_{31}$H$_{30}$PBr: C, 72.52; H, 5.89. Found: C, 72.34; H, 5.82.

***E*-[4-Br-2,6-Mes$_2$C$_6$H$_2$P═C(H)Ph] (3a).** A mixture of 0.15 g of 4-Br-2,6-Mes$_2$C$_6$H$_2$PCl$_2$ (0.30 mmol), 0.020 g of Zn dust (0.31 mmol), 32 μL of benzaldehyde (0.32 mmol), and 0.14 mL of neat PMe$_3$(1.74 mmol) in 20 mL of THF was allowed to stir for 6 h in a 50 mL round-bottom flask. The reaction mixture was then filtered, and the solvent was removed under vacuum. The remaining solid was rinsed with acetonitrile and then extracted into hexanes. The hexanes was removed under vacuum, and the pale yellow product was then recrystallized from a concentrated hexane solution at −35 °C to yield 0.12 g of yellow crystalline **3a** (75%). ^{1}H NMR (CDCl$_3$): δ 8.65 (d, $J_{PH} = 25.2$ Hz, 1H), 7.27 (s, 2H), 7.10 (s, 5H), 6.85 (s, 4H), 2.25 (s, 6H), 2.06 (s, 12H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 180.5 (d, $J_{PC} = 35.3$ Hz), 146.8 (d, $J_{PC} = 9.1$ Hz), 140.4 (d, $J_{PC} = 41.3$ Hz), 139.9 (d, $J_{PC} = 15.1$ Hz), 137.4 (s), 137.3 (s), 136.6 (d, $J_{PC} = 3.0$ Hz), 135.4 (s), 132.1 (s), 131.3 (s), 128.3 (s), 125.9 (d, $J_{PC} = 21.1$ Hz), 123.5 (s), 21.1 (s), 20.9 (d, $J_{PC} = 2.0$ Hz). ^{31}P{^{1}H} NMR(CDCl$_3$): δ 239.0. mp: 212−215 °C. UV−vis (CHCl$_3$): λ_{max} 337 nm, ($\epsilon = 16\,600$ M^{-1} cm^{-1}).

***E*-[4-Br-2,6-Mes$_2$C$_6$H$_2$P═C(H)C$_6$H$_4$Br] (4a).** A mixture of 1.0 g of 4-Br-2,6-Mes$_2$C$_6$H$_2$PCl$_2$ (2.0 mmol), 0.14 g of Zn (2.1 mmol), 0.39 g of *p*-bromobenzaldehyde (2.1 mmol), and 12.1 mL of a 1.0 M solution of PMe$_3$ in toluene (12.1 mmol) in 20 mL of THF was allowed to stir overnight in a 100 mL round-bottom flask. The reaction mixture was filtered and the solvent was removed under vacuum. The solid was rinsed with acetonitrile and then extracted in hexanes. The hexanes were removed under vacuum. The yellow product was recrystallized from a concentrated ether solution at −35 °C to give 0.51 g of yellow crystalline **4a** (45%). ^{1}H NMR (CDCl$_3$): δ 8.53 (d, $J_{PH} = 24.8$ Hz, 1H), 7.35 (s, 2H), 7.22 (d, $J_{HH} = 8.4$ Hz, 2H), 6.98−6.95 (m, 2H), 6.86 (s, 4H), 2.26 (s, 6H), 2.05 (s, 12H). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 240.5. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 178.7 (d, $J_{PC} = 35.4$ Hz), 146.7 (d, $J_{PC} = 8.5$ Hz), 140.0 (d, $J_{PC} = 39.7$ Hz), 138.8 (d, $J_{PC} = 14.8$ Hz), 137.5 (s), 136.9 (s), 135.4 (s), 131.5 (d, $J_{PC} = 2.5$ Hz), 131.4 (s), 128.3 (s), 127.2 (d, $J_{PC} = 21.5$ Hz), 123.7 (s), 122.1 (d, $J_{PC} = 8.5$ Hz), 21.1 (s), 20.9 (d, $J_{PC} = 2.1$ Hz). mp: 192−194 °C. UV−vis (CHCl$_3$): λ_{max} 345 nm, ($\epsilon = 30\,900$ M^{-1} cm^{-1}). Anal. Calcd for C$_{31}$H$_{29}$PBr$_2$: C, 62.86; H, 4.93. Found: C, 62.92; H, 4.70.

***Z*-[4-Br-2,6-Mes$_2$C$_6$H$_2$P═C(H)C$_6$H$_4$Br] (4b).** The isomerization of **4a** was conducted using a Rayonet photochemical reactor loaded with 350 nm UV source lamps. In a Pyrex NMR tube, 0.025 g of **4a** was dissolved in 0.7 mL of CDCl$_3$. The sample was exposed to the UV light for 6 h and then placed into the glovebox. After the solvent was removed under vacuum, the product was crystallized in a concentrated ether solution at −35 °C to yield 0.016 g of **4b** (60%). ^{1}H NMR (CDCl$_3$): δ 7.66 (d, $J_{PH} = 36.4$ Hz, 1H), 7.34 (s, 2H), 7.23 (d, $J_{HH} = 10$ Hz, 2H), 6.84 (m, 2H), 6.82 (m, broad, 4H), 2.26 (s, 6H), 2.02 (s, broad, 12H). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 235.4. mp: 176−178 °C. UV−vis (CHCl$_3$): λ_{max} 330 nm, ($\epsilon = 10\,200$ M^{-1} cm^{-1}).

Table 1. Crystal Data and Structure Refinement for **4a** and **4b**

empirical formula	C$_{31}$H$_{29}$Br$_2$P	C$_{31}$H$_{29}$Br$_2$P
fw	592.33	592.33
temp (K)	100(2)	100(2)
wavelength (Å)	0.71073	0.71073
cryst syst	orthorhombic	monoclinic
space group	*Fdd*2	*P*2$_1$/*c*
unit cell dimensions	$a = 25.9240(17)$ Å	$a = 17.8482(16)$ Å
	$b = 32.412(2)$ Å	$b = 9.6996(9)$ Å
	$c = 14.4521(2)$ Å	$c = 16.4619(14)$ Å
	$\alpha = 90°$	$\alpha = 90°$
	$\beta = 90°$	$\beta = 111.3850(10)°$
	$\gamma = 90°$	$\gamma = 90°$
vol (Å^3)	11143.1(13)	2653.7(4)
Z	16	4
density$_{calcd}$ (Mg/m^3)	1.412	1.483
abs coeff (mm^{-1})	2.984	3.133
F(000)	4800	1200
cryst size (mm)	0.30 × 0.30 × 0.20	0.25 × 0.20 × 0.15
crystal color/shape	pale yellow block	pale yellow block
θ range	1.84−27.50°	1.23−27.53°
limiting indices	$-28 < h < 33$	$-23 < h < 22$
	$-41 < k < 29$	$-12 < k < 12$
	$-15 < l < 16$	$-20 < l < 21$
reflns collected	12 813	22 059
independent reflns	5898 ($R_{int} = 0.0324$)	6000 ($R_{int} = 0.0452$)
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraint/params	5384/0/307	4757/0/307
GOF on F^2	0.990	1.028
Final R^a indices [$I > 2\sigma(I)$]	R1 = 0.0326	R1 = 0.0395
	wR2 = 0.0745	wR2 = 0.1001
R^a indices (all data)	R1 = 0.0366	R1 = 0.0550
	wR2 = 0.0758	wR2 = 0.1076

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and *a* and *b* are constants adjusted by the program.

Photolysis of 1a−3a. Photolysis of a **1a**−**3a** in CDCl$_3$ led to a mixture of **1a**−**3a** and **1b**−**3b**, as described in the text. For **1b**, ^{31}P{^{1}H} NMR (CDCl$_3$): δ 234.9. Partial ^{1}H NMR (CDCl$_3$): δ 7.57 d, $J_{PH} = 36.8$ Hz, 1H. For **2b**, ^{31}P{^{1}H} NMR (CDCl$_3$): δ 241.4. Partial ^{1}H NMR (CDCl$_3$): δ 7.66 (d, $J_{PH} = 36.0$ Hz, 1H). For **3b**, ^{31}P{^{1}H} NMR (CDCl$_3$): δ 229.8. Partial ^{1}H NMR (CDCl$_3$): δ 7.90 (d, $J_{PH} = 36.8$ Hz, 1H).

X-ray Diffraction Studies. Details for the data collection and structure solution are presented in Table 1. Further details may be found in the Supporting Information.

Computational Studies. Computations performed using the B3LYP hybrid functional[17] and a 6-31G+(d,p) basis set[18] using the Gaussian 03 suite of programs[19] on a PC platform. Full, unconstrained geometry optimizations were followed by TDDFT treatment of the optimized structures with the same functional and basis set. Frequency calculations conducted on optimized geometries indicated that the structures are minima because all of the frequencies have positive values. Full details are provided in the Supporting Information.

---

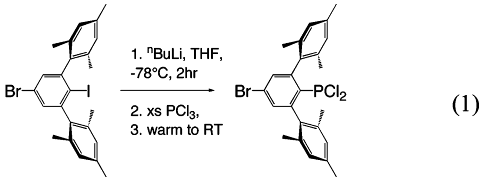
(17) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B.* **1988**, *37*, 785.

(18) Petersson, G. A.; Al-Laham, M. A. *J. Chem. Phys.* **1991**, *94*, 6081.

Results and Discussion

The chemistry of low-coordinate phosphorus compounds is now well-established, and a variety of groups are bringing increased attention to the development of such compounds for functional materials. The challenge for the synthetic chemist is the development of new bulky groups to allow both the stabilization of the low-coordinate atom and further chemical elaboration. One of the earliest successes was the report of a unique bulky group that allowed the preparation of a compound with two diphosphene units.[20] Later systems demonstrated the connection of redox-active groups in sites *para* to low-coordinate phosphorus compounds.[16,21] Systematic investigations of the impact of *para* substituents to phosphaalkene and diphosphene groups have also been reported.[22]

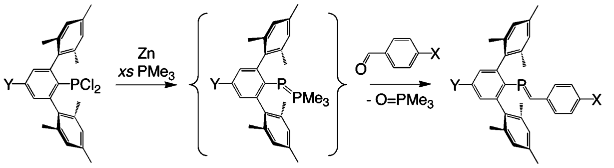
Our desire to develop new phosphaalkenes for remote functionalizaton led us to adopt a key intermediate from the work of Yoshifuji and workers.[16] Specifically, we were attracted to the *para*-bromo-substituted *meta*-terphenyl 4-Br-2,6-$Mes_2C_6H_2I$. In their work, it was shown that one can elaborate the less-hindered bromine atom position. Subsequent transformations could then introduce phosphorus into the protective pocket occupied by the iodine atom. By contrast, we needed to install a low-coordinate phosphorus into the hindered site first, and then later modify the less-hindered *para* position.



(1)

Normally, iodine would be expected to undergo metal−halogen exchange faster than bromine, thus the conventional routes to $ArPCl_2$ involving sequential reaction with ^nBuLi and PCl_3 could give the desired material. The steric coverage provided by the mesityl group, however, might make lithium−bromine exchange more favorable. Fortunately, the new dichloroarylphosphine $Ar'PCl_2$ (eq 1) was successfully isolated in a 32% yield by fairly standard procedures for preparing these types of hindered $ArPCl_2$.

Scheme 1



	1a	**2a**	**3a**	**4a**
Y =	H	Br	H	Br
X =	H	H	Br	Br

Synthesis of the three new phosphaalkenes (**2a**−**4a**) and known phosphaalkene **1a** (Scheme 1) took advantage of our version of the phospha-Wittig reaction.[15,23,24] The intermediate phospha-Wittig reagent was not isolated but was trapped in situ with the aldehyde in slight excess to give the desired phosphaalkene. Reactions were quantitative, analyzed by NMR spectroscopy, and yielded only the *E*-isomer of each pale yellow crystalline material. The new compounds were readily characterized by ^{31}P NMR shifts that were only by a few parts per million different from each other and previously reported **1a** (δ 239.0−245.7). All of these materials display characteristic doublets at δ 8.5−8.9 in their ^1H NMR spectra having very diagnostic coupling constants ($J_{PH} = 25$ Hz) for the *E* configuration about the phosphorus−carbon double bond.[6] Bromine atom substitution onto either or both ends of **1a** induces a red shift on the UV−vis spectra. The effects are additive, and the effect is greater when a single substitution is present on the less-hindered phenyl unit. This finding is consistent with the presumed greater ability of this ring to undergo conjugation with the phosphaalkene chromophore.

While compounds **1a**−**4a** are quite thermally stable in the absence of air and water, solutions of **1a**−**4a** exposed to room light showed evidence of the slow formation of significant quantities of their corresponding *Z* isomers, **1b**−**4b**. Most notably, an additional upfield signal in their ^{31}P NMR spectra and new doublets near 7.6 ppm in their ^1H NMR spectra with $J_{PH} = 36$ Hz strongly suggested partial conversion to the *Z* isomers. Conversions approached 84−90% using room light over an extended period of time (days). The process quickens if one tapes a NMR sample to a window to receive sunlight, or it can go even more rapidly, if one places samples in a Rayonet UV photochemical reactor (350 nm lamps). In the photochemical reactor, **1a**−**4a** undergo conversion to photostationary (pss) equilibria of 76−81% (by ^1H NMR) **1b**−**4b** over a 6 h period. Conducting the photolysis in a quartz EPR tube did not significantly change the position of the equilibrium, but the time for equilibration was reduced to 30 min. A solid sample of **1a** exposed to UV light for 6 h showed partial (30%) conversion to the **1b** isomer. It should be noted that in all of these

---

(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc.: Wallingford, CT, 2003.

(20) Yoshifuji, M.; Shinohara, N.; Toyota, K. *Tetrahedron Lett.* **1996**, *37*, 7815.

(21) Dutan, C.; Shah, S.; Smith, R. C.; Choua, S.; Berclaz, T.; Protasiewicz, J. D.; Geoffroy, M. *Inorg. Chem.* **2003**, *42*, 6241.

(22) (a) Kawasaki, S.; Nakamura, A.; Toyota, K.; Yoshifuji, M. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1110. (b) Termaten, A.; van der Sluis, M.; Bickelhaupt, F. *Eur. J. Org. Chem.* **2003**, 2049. (c) Smith, R. C.; Protasiewicz, J. D. *Eur. J. Inorg. Chem.* **2004**, 998.

(23) Shah, S.; Protasiewicz, J. D. *Coord. Chem. Rev.* **2000**, *210/1*, 181.

(24) For more phospha-Wittig chemistry, see: (a) Le Floch, P.; Marinetti, A.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1990**, *112*, 2407. (b) Le Floch, P.; Mathey, F. *Synlett* **1990**, 171.

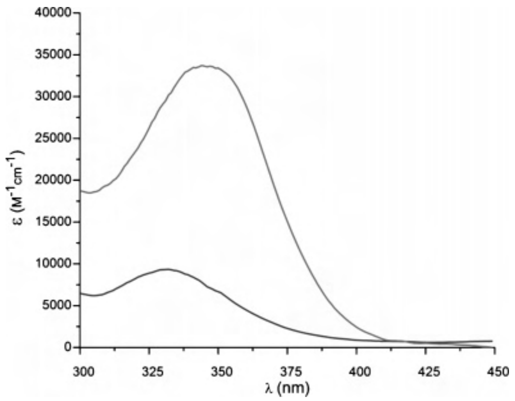


Figure 1. UV−vis spectra for **4a** (upper) and **4b** (lower) in $CDCl_3$.

experiments, no appreciable decomposition or loss of phosphaalkenes was noted. By comparison, the photoisomerization of E-Mes*P═C(H)Ph in solution using a medium-pressure mercury lamp yielded a mixture of E and Z phosphaalkenes in a 30:70 ratio.[6]

After photolysis of solutions of **4a**, we could isolate pure **4b** in a 60% yield. The UV−vis spectra of **4a** and **4b** are shown in Figure 1. Upon isomerization to the Z isomer, **4a** undergoes both a blue shift for its $\pi-\pi^*$ transition of 15 nm and a drop in intensity by a factor of 3. Using the absorption data at 350 nm for **4a** and **4b** ($\epsilon = 30\,300$ and 6920 $M^{-1}\ cm^{-1}$, respectively), one can use eq 2 to predict

$$\left(\frac{\text{cis}}{\text{trans}}\right)_{\text{pss}} = \frac{(\epsilon_{\text{trans}})}{(\epsilon_{\text{cis}})}\frac{(\Phi_{\text{trans}-\text{cis}})}{(\Phi_{\text{cis}-\text{trans}})} \qquad (2)$$

the cis/trans ratio produced with the light source in the photochemical reactor.[25] If one also assumes the quantum yields (Φ) for the photoisomerization reactions in both directions are equal, a cis/trans ratio of 0.23 is obtained, remarkably close to the ratio of 0.22 that is observed. Photolysis of pure **4b** in the photochemical reactor led to equilibration to a 24:76 ratio of **4a**/**4b** over a 6 h period. Heating a sample of pure **4b** in toluene at 80 °C for 15 h did not yield any detectable **4a**. A high thermal barrier is thus presumed for the E/Z isomerization process.

Single crystals of **4a** and **4b** grown from diethyl ether at −35 °C proved to be of sufficient quality for single-crystal X-ray analysis (Table 1). The results of the structural determinations rigorously confirm the E and Z assignments (Figures 2−4). Key metrical data for these compounds are listed in Table 2. The P═C(H)C_6H_4Br array in each compound lies between the cleft formed by the two outer mesityl rings, and thus they are not in optimized orientations for π-conjugation with the central benzene ring of the terphenyl units.

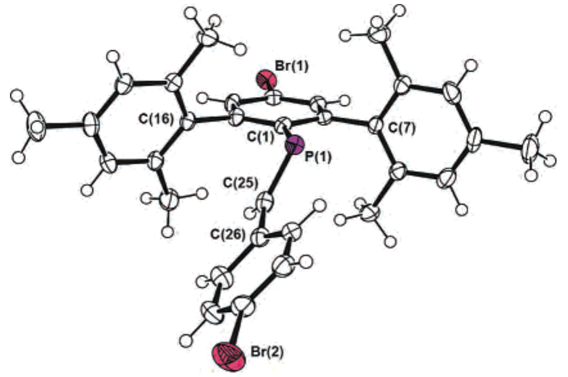


Figure 2. Structure of **4a**.

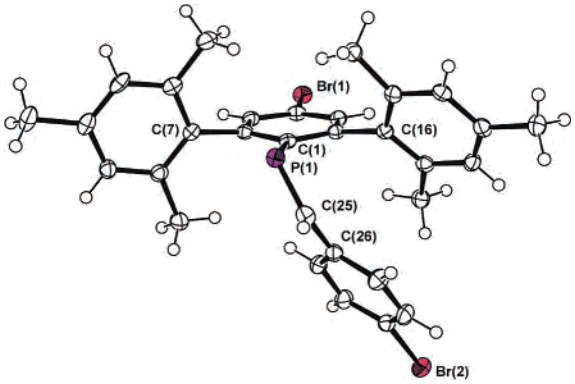


Figure 3. Structure of **4b**.

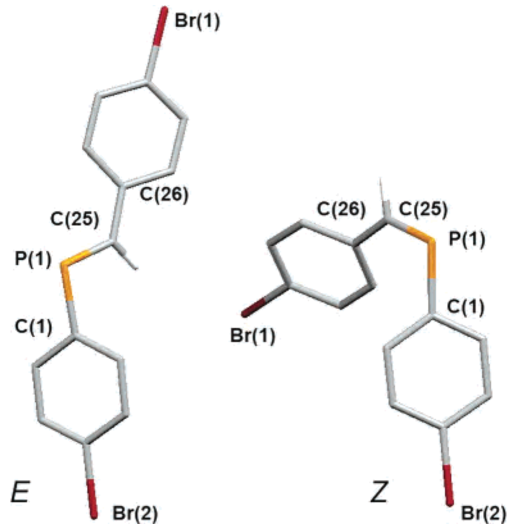


Figure 4. Simplified views of the structures of **4a** and **4b** emphasizing the configuration about double bonds (mesityl rings and most hydrogen atoms omitted for clarity).

The P═C bond length shortens by 0.016 Å on going from **4a** (1.682(3) Å) to **4b** (1.666(3) Å). Both of these values fall into the normal range of such values,[5,26] and they are longer than the P═C bond length of 1.634(3) Å reported for another *meta*-terphenyl phosphaalkene, E-ArP═C(H)Ph (Ar = 2,6-(2,6-$Cl_2C_6H_3)_2C_6H_3$).[27] A 5.7° larger C(25)−P(1)−C(1) bond angle (from 101.6(1)° to 107.3(1)°) appears upon conversion of the E isomer to its Z form. Likewise, the bond angle about C(25) increases by 11.8° (from 124.5(2)° to 136.3(2)°). This latter sizable increase may reflect some steric clashes between the bromophenyl ring and the mesityl rings. This notion is reinforced by noting that the C_{ipso} carbons of

---

[25] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper & Row Publishers: New York, 1981; p 298.

[26] (a) Appel, R.; Knoll, F. *Adv. Inorg. Chem.* **1989**, *33*, 259. (b) Markovskii, L. N.; Romanenko, V. D. *Tetrahedron* **1989**, *45*, 6019.

[27] Smith, R. C.; Ren, T.; Protasiewicz, J. D. *Eur. J. Inorg. Chem.* **2002**, 2779.

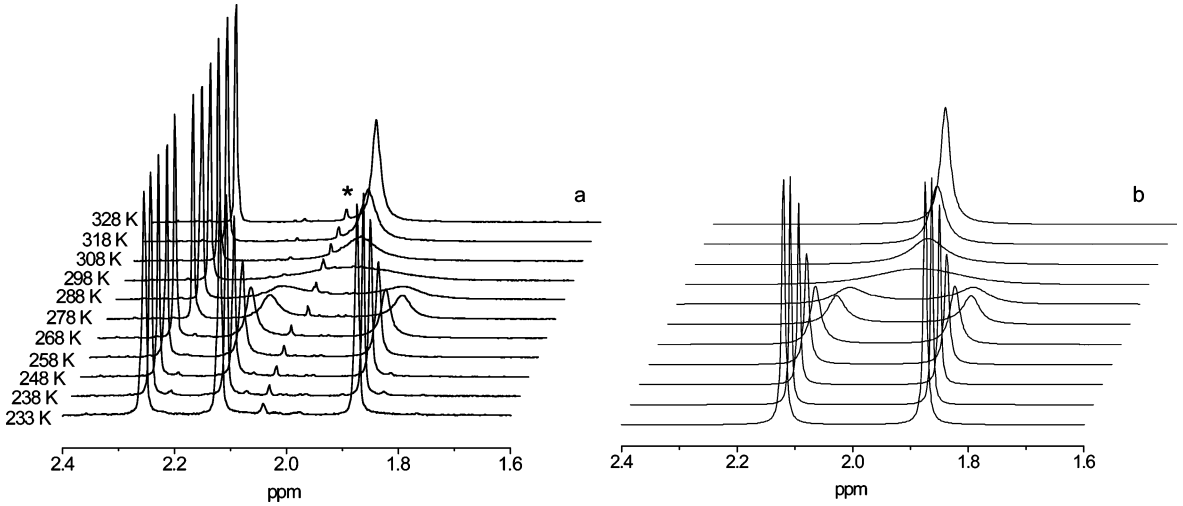
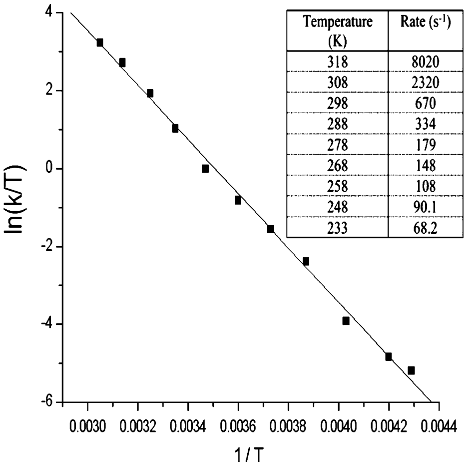


Figure 5. Temperature-dependent ^{1}H NMR (600 MHz) spectra **4b** in $CDCl_3$: (a) experimental (signal indicated by * from the small percentage of **4a**) and (b) simulated (WINDNMR).

Table 2. Selected Bond Distances (Å) and Angles (deg) for **4a** and **4b**

4a		4b	
P(1)−C(1)	1.842(3)	P(1)−C(1)	1.838(3)
P(1)−C(25)	1.682(3)	P(1)−C(25)	1.666(3)
C(25)−C(26)	1.453(4)	C(25)−C(26)	1.465(4)
Br(1)−C(4)	1.895(3)	Br(1)−C(4)	1.899(3)
Br(2)−C(29)	1.910(3)	Br(2)−C(29)	1.904(3)
C(25)−P(1)−C(1)	101.57(14)	C(25)−P(1)−C(1)	107.30(14)
C(6)−C(1)−C(2)	119.6(3)	C(2)−C(1)−C(6)	119.9(3)
C(26)−C(25)−P(1)	124.5(2)	C(26)−C(25)−P(1)	136.3(2)
C(6)−C(1)−P(1)	123.5(2)	C(6)−C(1)−P(1)	123.7(2)
C(2)−C(1)−P(1)	116.8(2)	C(2)−C(1)−P(1)	116.0(2)



Temperature (K)	Rate (s^{-1})
318	8020
308	2320
298	670
288	334
278	179
268	148
258	108
248	90.1
233	68.2

Figure 6. Eyring plot and rate data.

both mesityl rings lie approximately 0.21−0.22 Å above the plane of the central benzene ring of the terphenyl unit of **4b**, while the C_{ipso} atoms of the mesityl rings in **4a** are in the plane of the central benzene ring of the terphenyl unit.

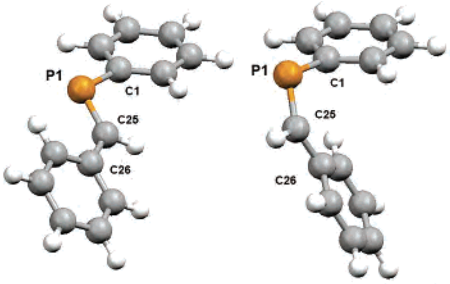
Structurally characterized *E*- and *Z*-Mes*P═C(H)Ph both display essentially identical P═C bond lengths.[6,28] In fact, the distances reported for the structures of *E*-Mes*P═C(H)-Ph (1.669−1.674 Å) bracket the value of 1.672 Å determined for the *Z* isomer. All of the atoms of the P═C(H)Ph unit lie in a single plane that is perpendicular to the Mes* aryl ring. The P═C(H)C_6H_4Br arrays in compounds **4a** and **4b**, however, appear to be less confined and CCP═C torsional angles are about 63°. For both *Z*-Mes*P═C(H)Ph and **4b**, the P═C−C bond angles have opened up by 13.7 and 11.8°, respectively, compared to their *E* isomers. A smaller increase in the C−P−C bond angles of 5.3−5.5° is noted in going from each pair of *E* to *Z* isomers.

Evidence of steric clashes and resultant hindered rotations is seen in the ^{1}H NMR spectrum of **4b**. The *ortho*-methyl resonances of **4a** are observed as a singlet, indicating rapid rotation about the P(1)−C(1) bond on the NMR time scale. The same protons for **4b** resonate as a broad signal at 2.0 ppm in $CDCl_3$. The *para*-methyl resonances of **4b**, however, appear as a sharp resonance at 2.26 ppm. Variable-temperature ^{1}H NMR studies of **4b** over the range of −40 to 55 °C reveal temperature-dependent behavior for the *ortho*-methyl signals (Figure 5, left). At the lowest temperature, two sharp signals are can be discerned, and at the highest temperature, a single resonance is resolved. These data were fit with a two site-exchange models (WINDNMR), yielding activation parameters of $\Delta H^‡ = 13.8$ kcal/mol and $\Delta S^‡ = 1.3$ eu (Figure 6). A parallel set of coalescence phenomenon were observed for the aromatic CH resonances of the mesityl groups, but these data were obscured by other overlapping signals and were not fit (but the estimated activation parameters were similar). These observations are all consistent with hindered rotation about the P−C^{Ar} bond of **4b**. As noted above, there are several features of the crystal structure suggesting steric pressures within **4b**. No temperature-dependent NMR spectra were reported for the related pair of phosphaalkenes *E*- and *Z*-Mes*P═C(H)Ph.[6] The *ortho*-*tert*-butyl groups of the Mes* group are reported as single resonances.

To better address the impact of steric forces in these isomers, we have conducted density functional theory (DFT) calculations on minimized structures of model compounds

---

(28) *d*(P═C) = 1.674(2) Å for *Z*-Mes*P═C(H)$C_6H_4NMe_2$, see: Romanenko, V. D.; Ruban, A. V.; Chernega, A. N.; Povolotskii, M. I.; Antipin, M. Y.; Struchkov, Y. T.; Markovskii, L. N. *Zh. Obsh. Khim.* **1989**, *59*, 1718.



P1-C1	1. 840 [1.842]	P1-C1	1. 850 [1.838]
P1-C25	1. 695 [1.682]	P1-C25	1. 693 [1.666]
C25-C26	1.461 [1.453]	C25-C26	1.465 [1.465]
C25-P1-C1	103.0 [101.6]	C25-P1-C1	107.8 [107.3]
C26-C25-P1	126.7 [124.5]	C26-C25-P1	138.0 [136.3]
Cn-C1-P1	117.0, 124.6 [116.8, 123.5]	Cn-C1-P1	119.2, 121.9 [116.0, 123.7]

Figure 7. Calculated structures and metrical data for PhP═C(H)Ph. For comparative purposes, experimentally determined values for **4a** and **4b** are given in brackets.

E- and *Z*-PhP═C(H)Ph.[29] The results shown in Figure 7 are in remarkable agreement with the experimentally determined structures considering that both the sterically demanding groups and the remote bromine atoms have been omitted. A small thermodynamic preference of 3.7 kcal/mol is calculated for the *E* isomer relative to the *Z* isomer. The *E* isomer deviates from noncoplanarity, presumably because of a steric clash between the hydrogen atom on C25 and the ortho proton on the nearby phenyl ring. The predicted P═C bond lengths of 1.695 and 1.693 Å are also consistent with the experimentally determined values for **4a** and **4b**. The calculations also provided information on the UV−vis transitions (Table 3). For each isomer, the HOMO−LUMO transition is predicted to be predominantly $\pi-\pi^*$ in character. Interestingly, for the *Z* isomer, there seems to be considerable mixing of the n and π orbitals and a drop in the predicted transition intensity (see Supporting Information). The $n-\pi^*$ transition is formally forbidden. Mixing with the allowed $\pi-\pi^*$ transition leads to intensity borrowing, a reduction of the $\pi-\pi^*$ intensity, and a concomitant increase in the $n-\pi^*$ transition. This result also correlates with the experimental absorption data (Figure 1).

Table 3. Properties Predicted for PhP═C(H)Ph by DFT

transition	energy (eV)	wavelength (nm)	oscillator strength
		trans	
$\pi \rightarrow \pi^*$	3.420	362.5	0.611
$n \rightarrow \pi^*$	4.042	306.7	0.037
		cis	
$\pi \rightarrow \pi^*$	3.559	348.4	0.188
$n \rightarrow \pi^*$	4.021	308.3	0.203

Conclusions

Three new *meta*-terphenyl-protected phosphaalkenes (**2**−**4**) have been prepared, and they and a previously characterized phosphaalkene (**1**) have been shown to undergo photoisomerization to *Z* isomers. Both the *E* and *Z* isomers of one of these new materials have been fully characterized, including single-crystal X-ray structural determinations. Variable-temperature NMR studies indicate that phosphorus−aryl bond rotation is hindered in the *Z* isomer of **4**. Computational studies have shed light on the relative importance of steric effects in determining the structures of the *E* and *Z* isomers of phosphaalkenes. In particular, the close agreement of the computed structures of *E*- and *Z*-PhP═C(H)Ph with those of **4a** and **4b** suggest that the bulky terphenyl can do its job to shelter the reactive P═C units but also allow the central ArP═C(H)Ar arrays to find conformations near what they might be in the absence of sterically demanding groups. Our work is ongoing to exploit these finding to prepare further unusual conjugated materials.

Acknowledgment. We thank the National Science Foundation (CHE-0202040 to J.D.P. and CHE-0518510 to M.C.S.) for support of this work.

Supporting Information Available: Crystallographic files in CIF format and details of the DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0520521

---

(29) Some related calculations on phosphaalkenes: (a) Nguyen, M. T.; Hegarty, A. F. *J. Chem. Soc., Perkin Trans. 2* **1985**, 2005. (b) Geoffroy, M.; Jouaiti, A.; Terron, G.; Cattani-Lorente, M.; Ellinger, Y. *J. Phys. Chem.* **1992**, *96*, 8241. (c) Schoeller, W. W.; Strutwolf, J.; Tubbesing, U.; Begemann, C. *J. Phys. Chem.* **1995**, *99*, 2329. (d) Schoeller, W. W.; Begemann, C.; Tubbesing, U.; Strutwolf, J. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2957.