Sterically Encumbered Systems for Two Low-Coordinate Phosphorus Centers

Shashin Shah,[†] Tom Concolino,[‡] Arnold L. Rheingold,[‡] and John D. Protasiewicz*,[†]

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106-7708, and
Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716-2522

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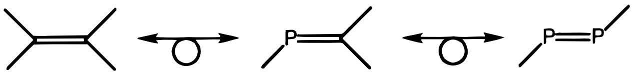
Tetraarylphenyls of the form 2,3,5,6-Ar_4C_6 (Ar = *p-tert*-butylphenyl) are investigated as sterically demanding ligands for the syntheses of compounds having two *p*-phenylene-bridged phosphorus centers. The precursor to such materials, 1,4-diiodo-2,3,5,6-tetrakis(*p-tert*-butylphenyl)benzene (**1**), is readily obtained via a one-pot procedure in 68% yield. Compound **1** is then used to provide the bis(dichlorophosphine) 1,4-bis(dichlorophosphino)-2,3,5,6-tetrakis(*p-tert*-butylphenyl)benzene (**2**) and the derived bis(phosphine) 1,4-bis(phosphino)-2,3,5,6-tetrakis(*p-tert*-butylphenyl)benzene (**3**) in yields of 56 and 94% respectively. These materials provide access to novel materials containing two low-coordinate phosphorus centers bridged by a sterically encumbered phenylene unit. Compound **2** reacts with benzaldehyde and 2,6-dichlorobenzaldehyde in the presence of excess trimethylphosphine and zinc to produce the new pale yellow crystalline bis(phosphaalkenes) (*E*,*E*)-PhC(H)=PAr_4C_6P=C(H)Ph (**4a**; 42%) and (*E*,*E*)-Ar′C(H)=PAr_4C_6P=C(H)Ar′ (**4b**; 46%; Ar′ = 2,6-dichlorophenyl). The crystal structure of **4a** shows a P=C bond length of 1.676(5) Å. Compound **2** is also used to provide the unusual red-orange bis(diphosphene) DmpP=PAr_4C_6P=PDmp (**5**; 55%; Dmp = 2,6-$Mes_2C_6H_3$). Compound **5** is structurally characterized, and a P=P bond length of 2.008(2) Å is ascertained.

Introduction

Phosphaalkenes and diphosphenes are isolobal analogues of olefins (Chart 1) bearing phosphorus atoms.[1−10] Upon the stepwise exchange of carbene for phosphinidene units, there arises an increasing need for the introduction of steric protective elements to allow the isolation of materials possessing increasingly reactive P=C and P=P bonds. In the absence of steric factors, PC and PP π bonds will often oligomerize to combinations of σ bonds (i.e., $(-PC-)_2$ or $(-PP-)_n$) due to thermodynamic preferences. Accompanying weaker π bonds are $\pi-\pi^*$ electronic transitions in the visible region of light. For example, while simple olefins are colorless, diphosphenes are yellow to orange. The relatively low lying π^* orbitals also make phosphaalkenes and diphosphenes susceptible to facile reduction to relatively stable radical anions. The ability to prepare these phosphorus analogues of olefins has been part of the basis for a greater appreciation of the relationships between the chemistry of C=C bonds and that of C=P and P=P bonds.[2] In fact, owing to the very similar electronegativities of carbon and phosphorus, P=C and P=P bonds are relatively nonpolar and behave like their all-carbon-based analogues. However, unlike their olefinic kin, compounds incorporating low-coordinate phosphorus atoms have not been systematically examined as building blocks for extended linear materials. One particular class of carbon-based oligomers and polymers that has been intensely studied is the poly(phenylenevinylenes) (PPV's, Chart 2).[11,12] These materials can be doped and display remarkable optical and electrical properties. Using the phosphorus−carbon analogy (Chart 1),[2] it can be envisioned that isolobal materials containing multiply bonded phosphorus centers can be constructed (Chart 2). Linking the known redox-active P=C and P=P functionalities via phenylene residues capable of offering pathways for electronic communication might also yield materials with interesting properties.

Chart 1



As mentioned above, the syntheses of stable phosphaalkenes and diphosphenes require the use of ligands that offer steric protection to these reactive units. For example, it was not until 1981 that an isolable material containing a true P=P double bond was reported.[13] In this particular case, stabilization of the diphosphene was achieved by use of the 2,4,6-tri-*tert*-butylphenyl group (Mes*). Many other sterically encumbered ligands have since been used to afford further examples of stable materials containing this functional unit. All of these sterically hindered groups prevent the thermodynamically favored oligomerization of the phosphinidene units of diphosphenes to cyclooligomers $(RP)_n$.

Although a variety of materials possessing multiple numbers of phosphaalkene units have appeared,[6,9] few such materials

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[†] Case Western Reserve University.

[‡] University of Delaware.

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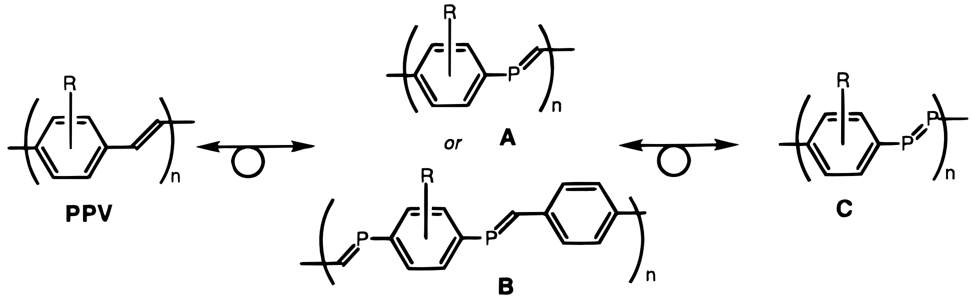
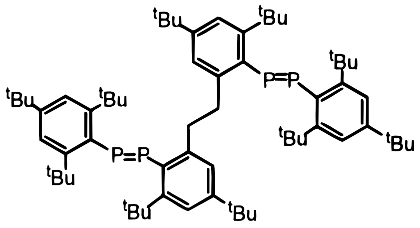
10.1021/ic0001558 CCC: $19.00

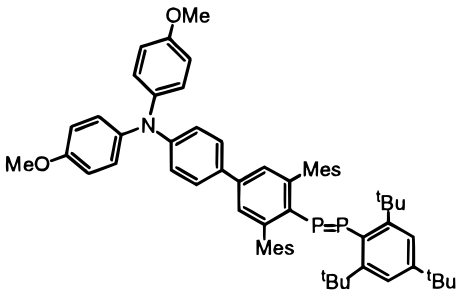
Chart 2



contain two low-coordinate phosphorus atoms bridged by a phenylene group.[14,15] A challenge to the generalized construction of materials that can incorporate multiple numbers of diphosphene or phosphaalkene units of the form presented in Chart 2 is the limited number of requisite difunctional benzenes that can simultaneously offer steric shelter for two multiply bonded phosphorus centers. In fact, the only known bis(diphosphene) is compound **I**.[16] This particular system, however, offers little possibility of allowing electronic communication between diphosphene units. An interesting diphosphene carrying a redox-active group was recently isolated and characterized (**II**), however.[17]

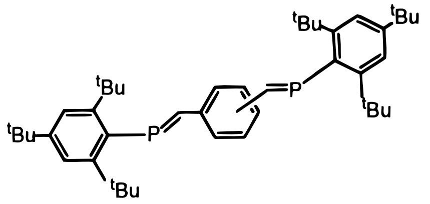


I



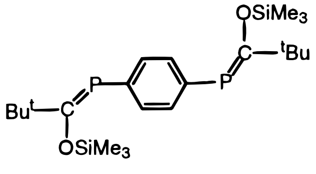
II

On the other hand, materials containing two phenylene-bridged phosphaalkene units are slightly more numerous and have received greater attention. Such materials are easier to prepare owing to the ready availability of fragments such as "Mes*P" and the lessened steric requirements for stabilizing the P=C group as compared to the P=P group (especially true for the group at the carbon atom). Of these materials, isomeric phenylene-bridged phosphaalkenes of the form $\{\mathrm{Mes^*P{=}C(H)}\}_n\mathrm{C_6H_{6-n}}$ (Mes* = 2,4,6-$^t\mathrm{Bu_3C_6H_2}$; n = 2−4) represent the most well studied systems.[18−25] In particular, the ortho, meta, and para isomers of $\{\mathrm{Mes^*P{=}C(H)}\}_2\mathrm{C_6H_4}$ (**IIIa−c**) have received careful attention. For example, a very recent study has shown that **IIIa−c** are more readily reduced to radical anions than their monosubstituted analogue Mes*P=C(H)Ph. The difference in reduction potentials was the largest for the para isomer ($\delta E \approx$ 354 mV).[25] Additionally, the radical anion derived from **IIIc** showed the unpaired spin to occupy a π^* orbital and also to be somewhat delocalized. Combined, these results suggest some degree of electronic communication between the P=C centers.



IIIa: *ortho*
IIIb: *meta*
IIIc: *para*

In contrast to **IIIa−c**, isomeric phosphaalkenes where a phenylene unit bridges two phosphorus atoms are rare. *p*-Phenylene-bridged phosphines are only well developed for the completely unhindered systems of the form 1,4-$\mathrm{(PX_2)_2C_6H_4}$.[18−24,26−28] Compound **IV** appears to be the sole example of a phosphaalkene with this sort of backbone.[14,29]



IV

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If further substituents could be incorporated into such materials, synthesis of a much wider range of interesting materials should be possible. We are thus pursuing the development of materials where two (or more) redox-active phosphorus atoms might communicate electronically through one or more sterically protected phenylene bridges. Materials possessing such stabilized low-coordinate centers could be used as building blocks for the construction of interesting oligomeric and/or polymeric materials containing multiply bonded inorganic elements. Herein we present a facile synthesis of a novel sterically encumbered ligand system that simultaneously provides stability to two low-coordinate phosphorus centers. Furthermore, we demonstrate that such new linker units can provide facile access to *both* bis(phosphaalkenes) and bis(diphosphenes), the first step toward materials of forms **B** and **C** in Chart 2.

Experimental Section

General Details. *p-tert*-Butylbromobenzene, hexabromobenzene, benzaldehyde, 1,4-terephthalaldehyde, and 2,6-dichlorobenzaldehyde were purchased from commercial sources. Benzaldehyde was distilled and then degassed with N_2, before being taken into a drybox for storage and use. *p-tert*-Butylbromobenzene was degassed with N_2, taken into the drybox, and passed through activated alumina before use. Hexabromobenzene and 2,6-dichlorobenzaldehyde were dried under vacuum and taken into the drybox for storage and use. DmpP═PDmp,[30] DmpP═C(H)Ph,[31] [DmpP(H)Li·Et$_2$O],[30] and DmpP═PMe$_3$[31] were prepared as previously described. Inert-condition manipulations were conducted in the drybox or on a Schlenk line under a nitrogen atmosphere. THF, toluene, hexanes, and diethyl ether were purified by distillation from purple or deep blue Na−benzophenone solutions under N_2. ^{1}H and ^{31}P NMR spectra were recorded using a 300 MHz Varian Gemini spectrometer. ^{31}P NMR data are referenced to external 85% H_3PO_4, while ^{1}H NMR data are referenced to residual proton solvent signals of $CDCl_3$ or C_6D_6. UV−vis spectra were obtained on a Varian Cary 5 spectrophotometer. Mass spectroscopic analyses were performed at the CWRU departmental facility.

1,4-Diiodo-2,3,5,6-tetrakis(*p-tert*-butylphenyl)benzene (1). A synthetic method similar to Hart's procedure was employed.[32] A 10.00 g sample of C_6Br_6 (18.1 mmol) was added to a freshly prepared Grignard solution of 4-^{t}BuC$_6$H$_5$MgBr (217 mmol) in 300 mL of THF. After the mixture was stirred overnight at room temperature, a white-brown precipitate was evident. The reaction was quenched dropwise with a solution of iodine in THF until a purple color (characteristic of excess iodine) persisted. Excess elemental iodine was consumed upon the addition of 1 M Na_2SO_3(aq). Then 500 mL of H_2O and 100 mL of diethyl ether were added, followed by separation of the organic and aqueous layers. The organic layer, which contained a suspension of the relatively insoluble compound **1**, was washed with three 100 mL portions of H_2O and then filtered to give crude **1** as a white solid. The white solid was washed successively with H_2O, EtOH, hexanes, and toluene to give 10.57 g of **1** (68%). ^{1}H NMR ($CDCl_3$): δ 7.11 (d, 8H, $^3J_{HH} = 8.3$ Hz), 6.91 (d, 8H, $^3J_{HH} = 8.3$ Hz), 1.21 (s, 36H). HRMS (FAB), *m*/*z*: calcd for $C_{46}H_{52}I_2$, 858.216 16; found, 858.220 14.

1,4-Bis(dichlorophosphanyl)-2,3,5,6-tetrakis(*p-tert*-butylphenyl)benzene (2). To a 500 mL Schlenk flask was added 5.00 g of **1** (5.82 mmol) in 250 mL of THF. The reaction flask was chilled to −78 °C, and 14.6 mL of ^{n}BuLi (23.4 mmol, 1.6 M in hexanes) was added dropwise by syringe. After the reaction mixture was stirred for 1 h at −78 °C, 8.00 g of PCl_3 (58.2 mmol) was rapidly added by syringe. The resulting mixture was allowed to slowly attain room temperature, after which it was stirred for 2 h. All volatiles were then removed under reduced pressure to give a yellow-brown solid, which was washed successively with CH_3CN and hexanes. The resultant solid was composed of **2** and LiCl. Extraction of **2** with hot toluene, followed by removal of all volatiles under reduced pressure, afforded 2.63 g of white **2** (56%). ^{1}H NMR (C_6D_6): δ 7.26 (d, 8H, $J = 8.3$ Hz), 7.10 (d, 8H, $J = 8.3$ Hz), 1.19 (s, 36H). ^{31}P NMR (C_6D_6): δ 153.9. HRMS (FAB), *m*/*z*: calcd for $C_{46}H_{52}P_2Cl_4$, 806.230 36; found, 806.233 77.

1,4-Bis(phosphanyl)-2,3,5,6-tetrakis(*p-tert*-butylphenyl)benzene (3). A solution of 2.0 g of **2** (2.47 mmol) in 200 mL of THF was slowly transferred via cannula to a solution of 422 mg of $LiAlH_4$ (11.3 mmol) in 100 mL of THF. The resulting suspension was refluxed for 1 h and then cooled to 0 °C. The reaction was carefully quenched with 5 equiv of a 20% HCl solution. Addition of 100 mL of Et_2O produced a two-phase mixture, and an insoluble white precipitate was apparent in the organic layer. The organic and aqueous layers were separated, and the former was filtered to give a white powder, which was washed with 50 mL of Et_2O and dried under reduced pressure. The dried solid was dissolved in THF, and the solution was filtered through a medium-porosity fritted glass filter layered with activated alumina. All volatiles were then removed under reduced pressure to give 1.56 g of white **3** (94%). ^{1}H NMR ($CDCl_3$): δ 7.13 (d, 8H, $J = 8.3$ Hz), 6.95 (d, 8H, $J = 8.3$ Hz), 3.29 (d, 4H, $J_{HP} = 216.8$ Hz), 1.21 (s, 36H). ^{31}P {^{1}H} NMR ($CDCl_3$): δ −130.9. HRMS (FAB), *m*/*z*: calcd for $C_{46}H_{56}P_2$, 670.386 08; found, 670.377 31.

(*E*,*E*)-1,4-Bis((phenylmethylidene)phosphino)-2,3,5,6-(tetrakis(*p-tert*-butylphenyl)benzene (4a) and (*E*,*E*)-1,4-Bis(((2,6-dichlorophenyl)methylidene)phosphino)-2,3,5,6-tetrakis(*p-tert*-butylphenyl)benzene (4b). A general procedure is described here for the syntheses of compounds **4a** and **4b**. Under inert conditions, a solution of 1.00 g of **2** (1.24 mmol) in 50 mL of THF was added slowly to a flask containing a mixture of zinc dust (202 mg, 3.09 mmol), the corresponding aldehyde (2.47 mmol, 2.0 equiv), and excess PMe_3 (14.8 mL of 1.0 M PMe_3 in toluene, 14.8 mmol) over a period of 15 min. The resulting yellow-orange solution was stirred for 2 h under ambient conditions and then filtered. All volatiles were removed under reduced pressure to give a yellow-orange solid. The yellow-orange solid was washed with ∼20 mL of hexanes and then extracted with a 1:1 mixture of Et_2O and toluene. All volatiles were again removed under reduced pressure, and the resulting solid was crystallized several times from toluene at −35 °C to give the pale yellow bis(phosphaalkene) **4a** (441 mg, 42%) or **4b** (562 mg, 46%). Experimental data for compound **4a** are as follows. ^{1}H NMR ($CDCl_3$): δ 8.50 (d, 2H, $^2J_{HP} = 25.6$ Hz), 6.95−7.08 (m, 26H), 1.14 (s, 36H). ^{31}P NMR ($CDCl_3$): δ 248.6. HRMS (FAB), *m*/*z*: calcd for $C_{60}H_{64}P_2$, 846.448 72; found, 846.451 50. UV−vis (THF): 349 nm ($\epsilon = 40\,000$). Experimental data for compound **4b** are as follows. ^{1}H NMR ($CDCl_3$): δ 8.51 (d, 2H, $^2J_{HP} = 25.1$ Hz), 7.14 (d, 4H, $J = 8.0$ Hz), 7.05 (m, 16H), 6.88 (t, 2H, $J = 8.0$ Hz), 1.16 (s, 36H). ^{31}P NMR ($CDCl_3$): δ 290.8. UV−vis for DmpP═C(H)-Ph (THF): 334 nm ($\epsilon = 63\,000$).

(*E*)-1,4-Bis(((2,6-dimesitylphenyl)phosphinidene)phosphino)-2,3,5,6-tetrakis(*p-tert*-butylphenyl)benzene (5). A solution of 1.00 g of **2** (1.24 mmol) in 100 mL THF was slowly added to a solution of [DmpP(H)-Li·Et$_2$O] (1.06 g, 2.48 mmol) in 50 mL of Et_2O. The resulting yellow solution was stirred for 2 h, after which DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) (373 mg, 2.45 mmol) was added, causing an immediate color change from yellow to orange and the formation of a white precipitate. The reaction mixture was stirred overnight under ambient conditions, and the volatiles were then removed under reduced pressure. The resulting orange-white solid was extracted with hexanes, and again all volatiles were removed under reduced pressure, giving an orange solid. Several recrystallizations from $CDCl_3$ at −35 °C afforded 925 mg of orange **5** (55%). ^{1}H NMR (C_6D_6): δ 7.05 (t, 2H, $J = 12.7$ Hz), 6.89 (s, 4H), 6.82−6.88 (m, 16H), 6.62 (d, 8H, $J = 12.6$ Hz), 2.31 (s, 12H), 1.87 (s, 24H), 1.12 (s, 36H). ^{31}P NMR ($CDCl_3$): δ 525.5 (d, $J_{PP} = 576$ Hz), 481.7 (d, $J_{PP} = 576$ Hz). HRMS (FAB), *m*/*z*: calcd for $C_{94}H_{102}P_4$, 1354.693 86; found, 1354.690 52. UV−vis (hexanes): 390 nm ($\epsilon = 7550$), 476 nm ($\epsilon = 870$). UV−vis DmpP═PDmp (hexanes): 456 nm ($\epsilon = 300$), 372 nm ($\epsilon = 4300$).

Crystallographic Structural Determinations. Single-crystal X-ray diffraction experiments were performed on a Siemens P4/CCD dif-

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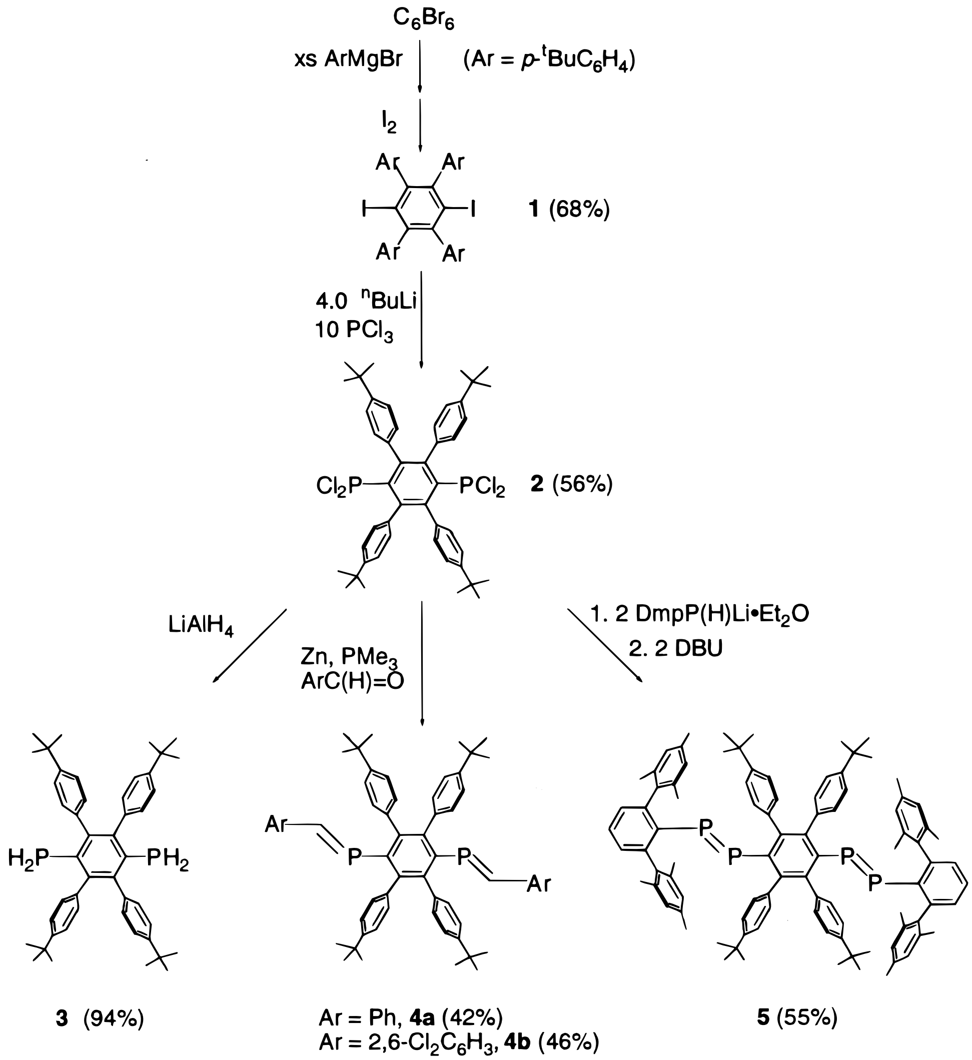
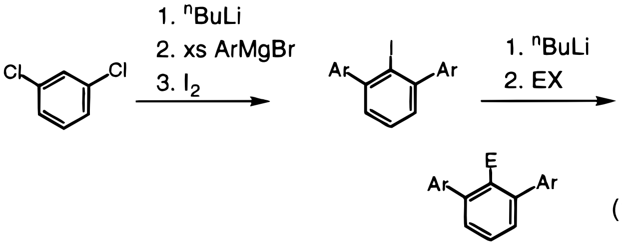
Scheme 1



fractometer for **4a** and **5**. The systematic absences and diffraction symmetry for **4a** were consistent with the tetragonal space groups $P4/n$ and $P4_2/n$. Solution in $P4_2/n$ yielded chemically reasonable and computationally stable results of refinement. No symmetry higher than triclinic was observed for the data of **5**. The E statistics suggested the centrosymmetric option $P\bar{1}$, which yielded chemically reasonable and computationally stable results of refinement. The asymmetric units of **4a** and **5** each contain one-half of the molecule lying about an inversion center. Compound **5** also contains one $CDCl_3$ solvate molecule per asymmetric unit. The structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined with anisotropic coefficients, and all hydrogen atoms were treated as idealized contributions. All software used and sources of the scattering factors were contained in the SHELXTL (5.03) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Results and Discussion

For our present purposes, we targeted tetraarylphenylene systems owing to their relative ease of synthesis and their apparently close relationship to the sterically encumbered *m*-terphenyl ligands that have already found widespread use in stabilizing multiply bonded phosphorus and other main group elements.[33] Attractive features of *m*-terphenyl ligands include their rapid synthesis from readily available and inexpensive dichlorobenzene and the wide range of aromatic groups that may be introduced (eq 1).[34] Fortuitously, tetraarylphenyls are essentially equally accessible from hexahalobenzenes, although this route is not quite as general for the introduction of aromatic groups.



(1)

Our synthesis of diiodotetraarylphenyls thus follows the methodology pioneered by Hart et al. (Scheme 1).[32] Unfortunately, efforts to find a high-yield synthesis of 1,4-diiodo-2,3,5,6-tetramesitylbenzene as a convenient entry to a difunctional analogue of the *m*-terphenyl ligand precursor 2,6-$Mes_2C_6H_3I$ (DmpI), which we have used successfully for the syntheses of the diphosphene DmpP═PDmp and a range of phosphaalkenes, DmpP═C(H)R,[30,31,35] have thus far failed. This particular reaction is plagued by competing side products that considerably diminish yields and hinder purifications.[36] Sys-

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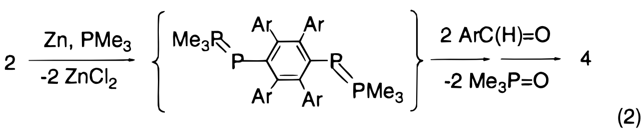
tematic investigations of 1,4-diiiodo-2,3,5,6-tetraarylphenyl syntheses have resulted in our immediate attention being directed toward 1,4-diiodo-2,3,5,6-tetrakis(*p*-*tert*-butylphenyl)benzene (**1**) as a precursor to phenylene-bridged ligands for phosphorus. This system offered several desirable features. First, compound **1** is easily prepared in a one-pot procedure and in good yields (Scheme 1, 68%). Second, our screening of 1,4-diiiodo-2,3,5,6-tetraarylphenyls revealed that it is important for the tetraaryl units incorporated into the phenylene group to bear a certain degree of aliphatic substituents. The four *tert*-butyl groups in **1** aid in promoting the solubility of what would otherwise be a relatively insoluble material due to highly packed aromatic groups. Oddly, although compound **1** itself displays limited solubility in organic media, the phosphorus derivatives **4a** and **5**, described below, are freely soluble. Third, analysis of reaction products by ^{1}H NMR spectroscopy is facilitated by the high symmetry of the system and the diagnostic resonances attributable to the *tert*-butyl groups. The incorporation of single substituents into either the meta or the ortho positions of the four aromatic rings leads to configurational isomerism.[32]

Conditions for dimetal for dihalogen substitution were optimized by reacting **1** with varying amounts of ^{n}BuLi, followed by treating reaction aliquots with aqueous solutions to produce 2,3,5,6-tetrakis(*p*-*tert*-butylphenyl)benzene. The addition of 4 equiv of ^{n}BuLi to **1** proved to be effective for this purpose. From freshly generated solutions of the dilithiated benzene, the bis(dichlorophosphine) **2** could be isolated in 56% yield after workup (Scheme 1). The yields were maximized by the rapid addition of PCl_3 during the transmetalation step. The ^{31}P NMR shift of δ 153.9 was unexceptional (compare $DmpPCl_2$ δ 160.4[30]). Reduction of **2** proceeded without difficulty by standard protocols to produce the bis(phosphine) **3** in excellent yield (Scheme 1). Compound **3** was readily characterized by a diagnostic triplet in the ^{31}P NMR spectrum at δ −130.9 (J = 217 Hz). Both **2** and **3** are white solids that are slightly air and water sensitive in the solid state.

Transformations of the bis(dichlorophosphine) **2** to bis(phosphaalkenes) **4a** and **4b** were rapidly accomplished using our recently described protocol for the construction of phosphaalkenes by zinc reduction of dichlorophosphines in the presence of aldehydes and excess trialkylphosphine.[31] A possible intermediate of the reaction, a bis(phosphanylidene-σ^4-phosphorane) (eq 2), could not be isolated. Using the more hindered Dmp ligand, we have isolated the related compound DmpP═PMe_3 and have shown that it reacts with aldehydes to produce phosphaalkenes DmpP═C(H)Ar.[31]



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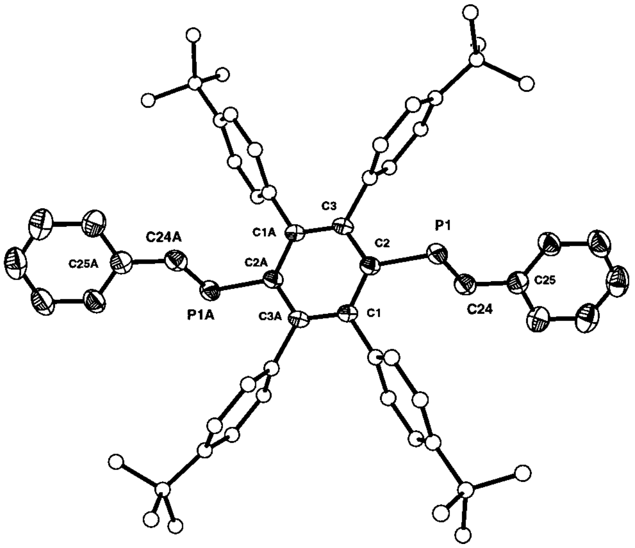

Figure 1. Structural diagram of compound **4a**.

^{31}P NMR analyses of the reaction mixtures show evidence for a single isomer of each phosphaalkene (**4a**, δ 248.6; **4b**, δ 290.8). The spectra of the isolated materials identify the configurations about the P═C bonds to be the bis-*E* isomers on the basis of the diagnostic $^{2}J_{PH}$ coupling constants of ∼25 Hz for the ArP═C(*H*)Ar′ protons.[37] Workup of the reaction mixtures provided the crystalline pale yellow bis(phosphaalkenes) **4a** and **4b** in 42−46% yields. The NMR properties of compounds **4a** and **4b** compare favorably with those reported for the isomeric phenylene-bridged phosphaalkenes of the form $\{Mes^*P{=}C(H)\}_nC_6H_{6-n}$ (**IIIa**−**c**).[18−25]

Recrystallization of **4a** from toluene at −35 °C produced single crystals suitable for X-ray diffraction studies, and the resulting structural solution is presented in Figure 1. Details of the structure solution and selected bond lengths and angles are found in Tables 1 and 2. The halves of **1** are related by a center of inversion. The P═C bond length of 1.676(5) Å falls within the general range observed for phosphaalkenes.[9] For example, the related bis(phosphaalkenes) **IIIa** and **IIIb** display P═C distances ranging from 1.656 to 1.670 Å. The *p*-bis(phosphaalkene) **IV**, likewise, shows similar P═C bond lengths of 1.683 Å.[29]

Of special interest is the orientation of the phenyl rings with respect to one another and with respect to the P═C unit. An ideal fully conjugated system would be all planar. Clearly, steric forces about the bridging phenylene group in **4a** might be expected to discourage an all-planar structure. Indeed, the hexasubstituted ring and each monosubstituted ring are offset from coplanarity by 62°. The great disparity in the steric demands for the groups capping each end of the P═C unit results in differences in these groups' abilities to attain coplanar orientations with the P═C unit. As such, the severities of these steric interactions are marked by a torsional angle of 71° for the P═C unit with the central ring and by torsional angles of 22° for the P═C unit with the outer benzaldehyde derived rings. Although the solid-state structure suggests that the rings are positioned about the P═C unit in this static manner, room-temperature NMR spectroscopy shows no evidence for this effect in solution.

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Table 1. Crystal Data and Structure Refinement Details for **4a** and **5**

	4a	**5**
empirical formula	$C_{60}H_{64}P_2$	$C_{96}H_{102}Cl_6D_2P_4$
fw	847.05	1596.38
temp (K)	223(2)	233(2)
λ (Å)	0.710 73	0.710 73
crystal system	tetragonal	triclinic
space group	$P4_2/n$	$P\bar{1}$
a, b, c (Å)	27.5025(2), 27.5025(2), 6.6317(2)	11.8495(2), 13.0427(2), 16.1474(2)
α, β, γ (deg)	90, 90, 90	89.3505(7), 75.9850(10), 74.4804(11)
V (Å^3), Z	5016.12(15), 4	2329.19(5), 1
d_{calcd} (Mg/m^3)	1.122	1.138
abs coeff (mm^{-1})	0.124	0.295
F(000)	1816	842
crystal size (mm)	0.45 × 0.45 × 0.20	0.30 × 0.20 × 0.15
θ range (deg)	2.09−24.50	1.30−23.00
limiting indices	$-32 < h < 27$ $-32 < k < 32$ $-6 < l < 7$	$-11 < h < 13$ $-14 < k < 13$ $-17 < l < 17$
no. of reflns collected	17 521	11 568
no. of indep reflns (R_{int})	4160 (0.0481)	6362 (0.0276)
completeness to θ (deg, %)	24.50, 99.6	23.00, 98.3
abs cor	empirical	empirical
max and min transm	0.9757 and 0.9465	0.9571 and 0.9166
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	4160/0/286	6362/0/490
goodness-of-fit on F^2	1.051	1.081
final R indices [$I > 2\sigma(I)$]: R1, wR2	0.0770, 0.1920	0.0932, 0.2348
R indices (all data):[a,b] R1, wR2	0.1022, 0.2179	0.1216, 0.2691
largest diff peak and hole (e Å^{-3})	0.677 and −0.256	0.698 and −0.499

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

Table 2. Bond Lengths (Å) and Angles (deg) for **4a**[a]

P(1)−C(24)	1.676(5)	C(24)−P(1)−C(2)	101.43(19)
P(1)−C(2)	1.847(4)	C(3)−C(2)−C(1)	120.0(3)
C(2)−C(3)	1.405(5)	C(3)−C(2)−P(1)	117.3(3)
C(2)−C(1)	1.407(5)	C(1)−C(2)−P(1)	122.6(3)
C(1)−C(3)^{i}	1.400(5)	C(3)^{i}−C(1)−C(2)	118.9(3)
C(3)−C(1)^{i}	1.400(5)	C(3)^{i}−C(1)−C(9)	120.6(3)
C(24)−C(25)	1.450(6)	C(1)^{i}−C(3)−C(2)	121.1(3)
		C(25)−C(24)−P(1)	124.8(3)

[a] Symmetry transformation used to generate equivalent atoms: (i) $-x, -y + 2, -z$.

The four aromatic rings about the bridging phenylene group are by necessity "stacked" upon one another and also appear to be "gear locked" in order to fit about the ring. Dihedral angles (τ) for the peripheral *p-tert*-butylphenyl rings relative to the core phenylene group are thus 70 and 78°. Similar structural features have been observed in other hindered tetraarylphenyls. For example, dihedral angles of 69 and 75° are realized for 2,3,5,6-tetraphenylphenol, a precursor to the tetraphenylphenoxide ligand, which has been employed as a cyclometalation-resistant ligand in organometallic chemistry.[38] Structures possessing related hindered phenylene units, such as tetraphenyl-*p*-benzoquinone ($\tau = 46$ and 72°) and the corresponding radical anions obtained by reduction of the benzoquinone with sodium (for the [Na(tetrapyran)$_2$] salt, $\tau = 55$ and 65°), have also been reported.[39]

As mentioned above, synthesis of a bis(diphosphene) requires greater steric protection than that of a bis(phosphaalkene). The bis(diphosphene) **5** was thus prepared to assay the ability of the tetrakis(*p-tert*-butylphenyl)phenylene group to stabilize two P═P bonds. Adaptation of literature methods for syntheses of asymmetric diphosphenes (Scheme 1) proved useful for this purpose.[40] Specifically, addition of 2 equiv of DmpP(H)Li•Et$_2$O (Dmp = 2,6-Mes$_2$C$_6$H$_3$) to **2**, followed by 2 equiv of DBU, led to **5** in 55% yield. Compound **5** was isolated as a stable red-orange material that was freely soluble in organic media. A pair of doublets resonating at δ 525.5 and 481.7 ppm ($J_{PP} = 576$ Hz) in the $^{31}P\{^1H\}$ NMR spectrum of **5**, in conjunction with the high symmetry of the ^{1}H NMR spectrum (i.e., a single set of *tert*-butyl resonances etc.) of **5**, suggested the presence of two P═P units connected by the phenylene bridge in a bis-*E* disposition.

The structure deduced from the NMR data was corroborated by the results of an X-ray diffraction study performed on a single crystal of **5**•2CDCl$_3$ grown from CDCl$_3$/hexanes at −35 °C (Figure 2). Details of the structure solution and selected bond lengths and angles are provided in Tables 1 and 3. As found for **4a**, the halves of **5** are related by a center of inversion. The P═P bond length of 2.008(2) Å falls within the range anticipated for phosphorus−phosphorus double bonds.[16,17] Structural parameters for the hindered linking unit of **5** are comparable to those observed for **4a**. For example, dihedral angles of 68 and 70° are seen for the peripheral *p-tert*-butylphenyl rings relative to the core phenylene group. The bis(diphosphene) **5** is formally related to the diphosphene DmpP═PDmp[30] by insertion of the bis(phosphinidene) fragment PArP (Ar = 2,3,5,6-(*p*-^{t}BuC$_6$H$_4$)$_4$C$_6$) into the PP double bond of DmpP═PDmp. The capping DmpP groups are thus structurally orientated in a fashion very similar to that found in DmpP═PDmp. In the solid state of DmpP═PDmp, the two *m*-terphenyl groups are organized such that one ring is nearly coplanar with the P═P unit while the other ring is nearly orthogonal to this unit (torsional angles of 81 and 13°,

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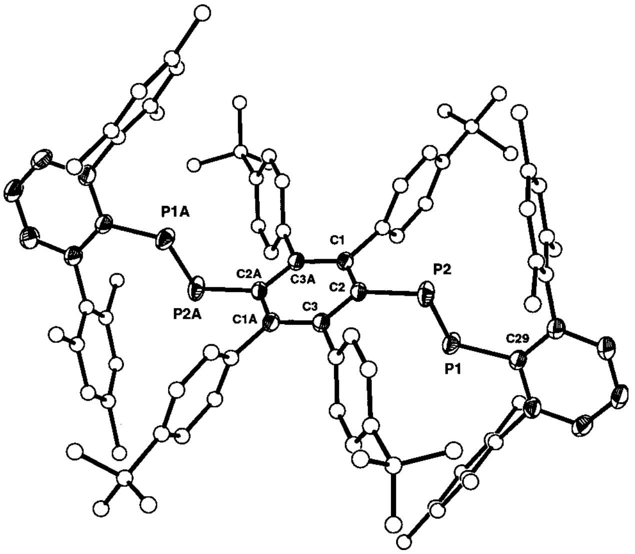

Figure 2. Structural diagram of compound **5**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **5**[a]

P(1)−C(29)	1.843(5)	C(29)−P(1)−P(2)	106.30(18)
P(1)−P(2)	2.008(2)	C(2)−P(2)−P(1)	97.52(16)
P(2)−C(2)	1.854(5)	C(2)−C(1)−C(3)^i	119.8(4)
C(1)−C(2)	1.401(7)	C(1)−C(2)−C(3)	120.3(4)
C(1)−C(3)^i	1.402(7)	C(1)−C(2)−P(2)	121.6(4)
C(1)−C(9)	1.507(7)	C(3)−C(2)−P(2)	118.1(4)
C(2)−C(3)	1.407(7)	C(1)^i−C(3)−C(2)	119.9(4)
C(3)−C(1)^i	1.402(7)		

[a] Symmetry transformation used to generate equivalent atoms: (i) $-x + 1, -y + 1, -z$.

respectively). For **5**, the torsional angles for the central and end-capping rings are 84 and 30°, respectively. The NMR spectra of **5** under ambient conditions suggest that rotation about the aryl−phosphorus bonds is facile on the NMR time scale.

With the solid-state structures of **4a** and **5** determined, it was of interest to assay the potential degree of electronic communication between the unsaturated organophosphorus groups within **4a** and **5**. If the two P═C or two P═P units are conjugated, then it might be expected that there would be a decrease in the energy required to promote electrons from the π to π^* orbitals for these functional groups. Compounds **4a** and **4b** are pale yellow, whereas phosphaalkenes of the form ArC(H)═PAr′ are often colorless, suggesting some electronic influence of the second P═C unit on the first. A more quantitative (but still inexact) measure of this effect is the UV−visible spectrum of **4a** compared to that of a closely related monofunctional analogue, DmpP═C(H)Ph (Figure 3, λ_{max} = 334 nm).[31] The absorption maximum for **4a** (λ_{max} = 349 nm) is red shifted by 15 nm. This notable shift is close to the red-shift of 11 nm reported between the mono(phosphalkene) Mes*P═C(H)Ph (λ_{max} = 315 nm) and the bis(phosphaalkene) **IIIc** (λ_{max} = 326 nm).[24]

Likewise, similar measurements for **5** have been performed (Figure 4). Two bands are readily discerned for **5** at λ_{max} = 390 and 476 nm. These two transitions, often observed for diphosphenes, have been assigned to $\pi \rightarrow \pi^*$ and $n^+ \rightarrow \pi^*$ electronic transitions, respectively (n^+ is the MO for the in-phase combination of lone pairs on P atoms). The latter transition is formally forbidden and is less intense than the allowed $\pi \rightarrow \pi^*$ transition.[5] Various computational efforts have indicated that the n^+ and the π MO's are very close in energy.[41,42] To gauge any potential electronic communication between the two P═P units, the electronic spectrum of DmpP═PDmp (λ_{max} = 372 and 456 nm) is also shown in Figure 4. Using this particular diphosphene as the closest available structurally related model, red shifts on the order of 18−20 nm can be estimated for *both* transitions upon moving from DmpP═PDmp to **5**. Such a result could be rationalized if the presence of the second P═P unit either lowers the energy of the π^* MO or raises the energy of *both* the n^+ and the π MO's. In this regard, it is important to note that comparisons between the electronic spectra of Mes*P═PMes* (λ_{max} = 340 and 460 nm) and $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ (λ_{max} = 353 and 484 nm) have led to the conclusion that there is minimal conjugation of the P═P unit with the phenyl rings of Mes*P═PMes*.[10] Comparisons of this sort are made much more difficult because of the massive sizes of these ligands and their resulting nonplanar structures. Even the simple addition of methyl substituents at the 2,2′,4,4′,6,6′-positions of stilbene results in a disruption of conjugation and a blue shift of nearly 30 nm [43] Future investigations of the cyclic voltammetry of **4** and **5**, as well as EPR spectroscopy of the radical anions derived by reduction of **4** and **5**, will help illuminate further details of the electronic nature of these difunctional materials.

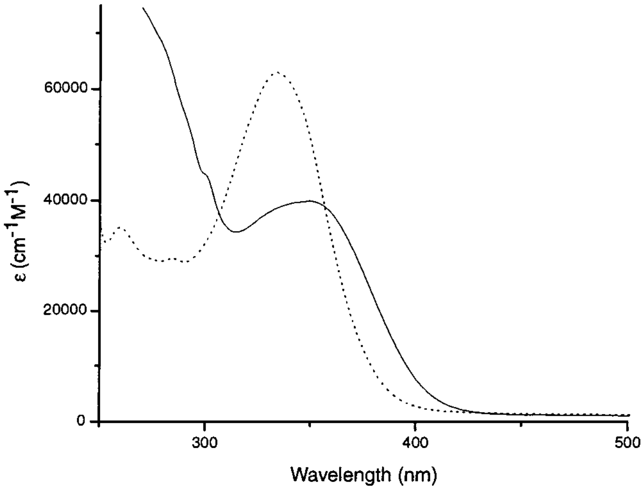

Figure 3. UV−visible spectra of DmpP═C(H)Ph (dashed line) and **4a** (solid line) in THF.

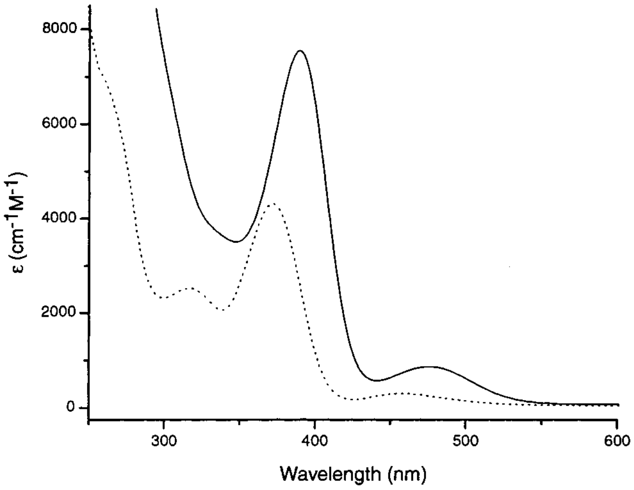

Figure 4. UV−visible spectra of DmpP═PDmp (dashed line) and **5** (solid line) in THF.

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Conclusions

Routes to sterically demanding ligands that provide access to materials having two low-coordinate phosphorus centers spanning a phenylene unit have been developed. In particular, new bis(phosphaalkenes) and bis(diphosphenes) based on these ligands have been prepared and structurally characterized. The bis(diphosphene) **5** represents only the second compound to bear two diphosphene units and is the first such species to be structurally characterized. Furthermore, these systems show evidence in their UV−visible spectra for red shifts on the order of 15−20 nm. These data also suggest that, in solution, the steric forces in **4a** and **5** do not completely isolate the two P═C or two P═P units from electronic communication. Further work to use these sterically encumbered tetraarylphenyls in more extended organophosphorus systems is currently underway. Hindered ligands of this type should also find applications in other areas of inorganic chemistry. In particular, such tetraarylphenyl ligands should lead to the facile development of materials having other types of novel main group multiple bonds, in much the same way that the use of *m*-terphenyl groups as sterically encumbered ligands has grown.

Acknowledgment. We thank the National Science Foundation (Grant CHE-9733412) for support of this research.

Supporting Information Available: More completely labeled ORTEP diagrams and tables listing atomic positional parameters, thermal parameters, and bond lengths and angles for **4a** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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