

# Syntheses and Structural Characterizations of the Unsymmetrical Diphosphene $\text{DmpP}=\text{PMes}^*$ ( $\text{Dmp} = 2,6\text{-Mes}_2\text{C}_6\text{H}_3$ , $\text{Mes}^* = 2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2$ ) and the Cyclotetraphosphane $[\text{DmpPPPh}]_2$

Rhett C. Smith,<sup>†</sup> Eugenijus Urnezis,<sup>†</sup> Kin-Chung Lam,<sup>‡</sup> Arnold L. Rheingold,<sup>‡</sup> and John D. Protasiewicz<sup>\*†</sup>

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

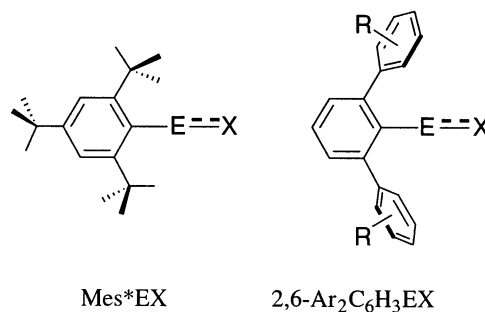
Received May 30, 2002

The new diphosphene  $\text{DmpP}=\text{PMes}^*$  ( $\text{Dmp} = 2,6\text{-Mes}_2\text{C}_6\text{H}_3$ ;  $\text{Mes}^* = 2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2$ , **1**) having two different classes of sterically demanding aryls has been prepared and structurally characterized. This structure appears to be the first featuring both types of sterically demanding groups (a *meta*-terphenyl and  $\text{Mes}^*$ ) in a single molecule about a multiply bonded unit. Compound **1** features a P=P bond length of 2.024(13) Å. The structure of **1** also allows comparisons to the two previously structurally characterized symmetric diphosphenes  $\text{DmpP}=\text{PDmp}$  and  $\text{Mes}^*\text{P}=\text{PMes}^*$ . The crystal structure of the cyclotetraphosphane  $[\text{DmpPPPh}]_2$  (**3**), the product of self-dimerization of the unstable diphosphene  $\text{DmpP}=\text{PPh}$  (**2**), has been determined. The structure of **3** demonstrates that a single bulky *Dmp* group is insufficient to prevent dimerization of **2**. <sup>31</sup>P NMR data for all three compounds are also reported.

## Introduction

The use of the  $\text{Mes}^*$  unit ( $\text{Mes}^* = 2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2$ , Chart 1, left) as a sterically demanding group in organophosphorus chemistry has led to many significant discoveries of new compounds containing multiply bonded phosphorus atoms. For example, a bona fide phosphobenzene was not realized until 1981 with the synthesis of  $\text{Mes}^*\text{P}=\text{PMes}^*$ .<sup>1</sup> As was shown in this and in following studies, successful isolation of diphosphenes ( $\text{RP}=\text{PR}$ ) necessitates the use of sterically bulky groups to thwart redistribution reactions of the constituent phosphinidene ( $\text{RP}$ ) fragments to cyclooligomeric products.<sup>2</sup> More recently, the use of *meta*-terphenyl ligands ( $2,6\text{-Ar}_2\text{C}_6\text{H}_3$ , Chart 1, right) has proven to be equally effective in providing steric shielding for new and exciting compounds having multiply bonded phosphorus and other main group elements.<sup>3,4</sup> We are currently interested in developing *meta*-terphenyl, and the related tetraphenyl

Chart 1



ligands ( $2,3,5,6\text{-Ar}_4\text{C}_6$ ), for the synthesis of molecules incorporating multiple low-coordinate phosphorus centers.<sup>5</sup> Herein we present the synthesis of two new diphosphenes  $\text{DmpP}=\text{PR}$  ( $\text{Dmp} = 2,6\text{-Mes}_2\text{C}_6\text{H}_3$ ;  $\text{R} = \text{Mes}^*$  (**1**),  $\text{Ph}$  (**2**)) having differing degrees of stability. The single-crystal X-ray structure of the stable asymmetric diphosphene  $\text{DmpP}=\text{PMes}^*$

\* To whom correspondence should be addressed. E-mail: jdp5@po.cwrw.edu.

<sup>†</sup> Case Western Reserve University.

<sup>‡</sup> University of Delaware.

(1) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587.

(2) Weber, L. *Chem. Rev.* **1992**, *92*, 1839.

(3) Recent reviews: (a) Twamley, B.; Haubrich, S. T.; Power, P. *Adv. Organomet. Chem.* **1999**, *1*. (b) Clyburne, J. A. C.; McMullen, N. *Coord. Chem. Rev.* **2000**, *210*, 73.

(4) For recent discussion of kinetic and thermodynamic aspects of stabilization by sterically encumbered groups, see: Burford, N.; Clyburne, J. A. C.; Chan, M. S. W. *Inorg. Chem.* **1997**, *36*, 3204.

(5) Shah, S.; Concolino, T.; Rheingold, A. L.; Protasiewicz, J. D. *Inorg. Chem.* **2000**, *39*, 3860.

is reported, which appears to be the first structurally characterized material featuring both types of sterically demanding groups (a *meta*-terphenyl and Me<sup>s</sup>\*) in a single molecule about a multiply bonded unit. In addition, the crystal structure of the cyclotetraphosphane [DmpPPP<sub>2</sub>]<sub>2</sub> (**3**), the product of self-dimerization of the unstable diphosphene DmpP=PPh, has also been determined.

## Experimental Section

**General Procedures.** All manipulations were carried out by using modified Schlenk techniques or in a drybox under N<sub>2</sub>. Solvents were purified by distillation from Na–benzophenone ketyl under a N<sub>2</sub> atmosphere before use. PhPCl<sub>2</sub> was distilled and degassed prior to use. DmpPCl<sub>2</sub>,<sup>6</sup> DmpPH<sub>2</sub>,<sup>6</sup> and Me<sup>s</sup>\*PH<sub>2</sub><sup>7</sup> were prepared by reported methods. NMR data were recorded on a Varian Gemini spectrometer operating at 300 MHz or 121 MHz for <sup>1</sup>H and <sup>31</sup>P spectra, respectively. <sup>31</sup>P NMR data are referenced to external 85% H<sub>3</sub>PO<sub>4</sub>, while <sup>1</sup>H NMR data are referenced to residual proton solvent signals of CDCl<sub>3</sub>. Mass spectroscopic analyses were performed at the CWRU departmental facility.

**DmpP=PMe<sup>s</sup>\* (1).** A solution of 0.10 g of [Li(Et<sub>2</sub>O)][P(H)-Me<sup>s</sup>\*] (0.29 mmol) in 10 mL of diethyl ether was added to a solution of 0.12 g of DmpPCl<sub>2</sub> (0.29 mmol) in 10 mL of diethyl ether with stirring over a 30 min period. During that time a fine white precipitate formed. The solvent was reduced in volume to 10 mL, and a solution of 0.044 g of DBU (0.29 mmol) in 2 mL of diethyl ether was added. Upon addition, the solution became yellow and eventually became orange over a 1 h period, after which time the reaction mixture was filtered and the solvent was removed in vacuo. The solid material was recrystallized from hexanes at –35 °C to give 0.091 g of yellow crystalline **1** (50%). <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ 526.2 (d, *J*<sub>PP</sub> = 572 Hz), 455.5 (d, *J*<sub>PP</sub> = 572 Hz). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.99 (s, 18H), 1.27 (s, 9H), 2.11 (s, 12H), 2.30 (s, 6H), 6.85 (s, 4H), 6.97 (s, 2H), 7.04 (d, 2H, *J*<sub>HH</sub> = 8 Hz), 7.43 (t, 1H, *J*<sub>HH</sub> = 8 Hz). HRMS (FAB, M+1): calcd for C<sub>42</sub>H<sub>55</sub>P<sub>2</sub>, 621.3779; found, 621.3790.

**[DmpPPP<sub>2</sub>]<sub>2</sub> (3).** A solution of 0.24 g of [Li(Et<sub>2</sub>O)][P(H)Dmp] (0.56 mmol) in 30 mL of Et<sub>2</sub>O was added to a vigorous stirred solution of 0.10 g of PhPCl<sub>2</sub> (0.56 mmol) in 20 mL of diethyl ether over a 30 min period. During this time a fine white precipitate was formed. After an additional 1 h of vigorous stirring, a <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of an aliquot indicated complete consumption of PhPCl<sub>2</sub>. The solvent was reduced in volume to 25 mL. To the resulting white suspension was added a solution of 0.086 g of DBU (0.56 mmol) in 10 mL of diethyl ether. The solution became yellow, and analysis of a reaction aliquot by <sup>31</sup>P NMR spectroscopy immediately after the addition of DBU showed the presence of only the diphosphene DmpP=PPh (**2**, δ 492.3 (d, *J*<sub>PP</sub> = 575 Hz), 489.2 (d, *J*<sub>PP</sub> = 575 Hz)). After 1 h, the reaction mixture was filtered and the solvent removed in vacuo to give 0.215 g of **3** (82%). <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ –24.8 (t, *J*<sub>PP</sub> = 120 Hz), –44.4 (t, *J*<sub>PP</sub> = 120 Hz). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.75 (s, 24H), 2.09 (s, 12H), 6.46 (s, 8H), 6.70 (d, 4H, *J*<sub>HH</sub> = 8 Hz), 7.00–7.20 (m, 12H). HRMS (FAB): calcd for C<sub>60</sub>H<sub>60</sub>P<sub>4</sub>, 904.3646; found, 904.3639.

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

**Table 1.** Crystal Data and Structure Refinement for **1** and **3**

param	<b>1</b>	<b>3</b>
empirical formula	C <sub>42</sub> H <sub>54</sub> P <sub>2</sub>	C <sub>62</sub> H <sub>64</sub> O <sub>0.50</sub> P <sub>4</sub>
fw	620.79	941.01
temp (K)	173(2)	293(2)
wavelength (Å)	0.710 73	0.710 73
cryst system	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
unit cell dimens (Å, deg)	<i>a</i> = 12.2774(2) <i>b</i> = 13.1536(2) <i>c</i> = 14.4521(2) $\alpha$ = 63.6983(6) $\beta$ = 80.3553(7) $\gamma$ = 64.1540(5)	<i>a</i> = 12.4811(13) <i>b</i> = 13.0376(13) <i>c</i> = 21.9996(2) $\alpha$ = 80.933(8) $\beta$ = 78.112(7) $\gamma$ = 62.186(6)
<i>V</i> (Å <sup>3</sup> )	1882.04(4)	2809.0(5)
<i>Z</i>	2	2
density (calcd, Mg/m <sup>3</sup> )	1.095	1.113
abs coeff (mm <sup>-1</sup> )	0.142	0.172
<i>F</i> (000)	672	1000
cryst size (mm)	0.40 × 0.20 × 0.20	0.14 × 0.14 × 0.34
cryst color and shape	yellow-orange block	colorless prism
$\theta$ range data collcn (deg)	1.84–22.50	1.99–24.50
limiting indices	13 < <i>h</i> < 13 14 < <i>k</i> < 13 15 < <i>l</i> < 15	1 < <i>h</i> < 14 13 < <i>k</i> < 14 22 < <i>l</i> < 22
reflcs colled	4728	10 151
indpt reflcs	4040 ( <i>R</i> <sub>int</sub> = 0.0448)	8782 ( <i>R</i> <sub>int</sub> = 0.0423)
refinement method	full-matrix least squares on <i>F</i> <sup>2</sup>	full-matrix least squares on <i>F</i> <sup>2</sup>
data/restraint/params	4728/0/397	8782/0/599
goodness-of-fit on <i>F</i> <sup>2</sup>	1.947	1.080
final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0706 <i>wR</i> <sub>2</sub> = 0.1977	<i>R</i> <sub>1</sub> = 0.0770 <i>wR</i> <sub>2</sub> = 0.2072
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0843 <i>wR</i> <sub>2</sub> = 0.2113	<i>R</i> <sub>1</sub> = 0.1504 <i>wR</i> <sub>2</sub> = 0.2450

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

## Results and Discussion

A variety of synthetic routes have been applied to the preparation of asymmetric diphosphenes (RP=PR'). For the present compounds, the best route involved performing the first step of the condensation by reaction of a phosphanido salt [Li(Et<sub>2</sub>O)][P(H)Ar] with Ar'PCl<sub>2</sub> (Scheme 1).

Reactions were then monitored by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy to ensure full consumption of Ar'PCl<sub>2</sub> prior to addition of DBU. Addition of DBU to these solutions thus readily promotes dehydrochlorination of the diphosphines R(H)PP(Cl)R' to cleanly yield the diphosphenes **1** and **2**, as judged by <sup>31</sup>P NMR spectroscopy. Diphosphene **1** is also produced as a major product during photolysis of mixtures of DmpP=PMe<sub>3</sub> and Me<sup>s</sup>\*P=PMe<sub>3</sub>.<sup>8</sup> In comparison to known asymmetric diphosphenes, both the chemical shifts and the magnitudes of PP coupling constants are in the normal range for **1** and **2**.<sup>2</sup> For example, the diphosphene 4-{NAr<sub>2</sub>}-2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>2</sub>P=PMe<sup>s</sup>\* (Ar = 4-MeOC<sub>6</sub>H<sub>4</sub>), the first example of a terphenyl- and Me<sup>s</sup>\*-protected π-bonded species, shows δ 453 and 530 (*J*<sub>PP</sub> = 575 Hz).<sup>9</sup>

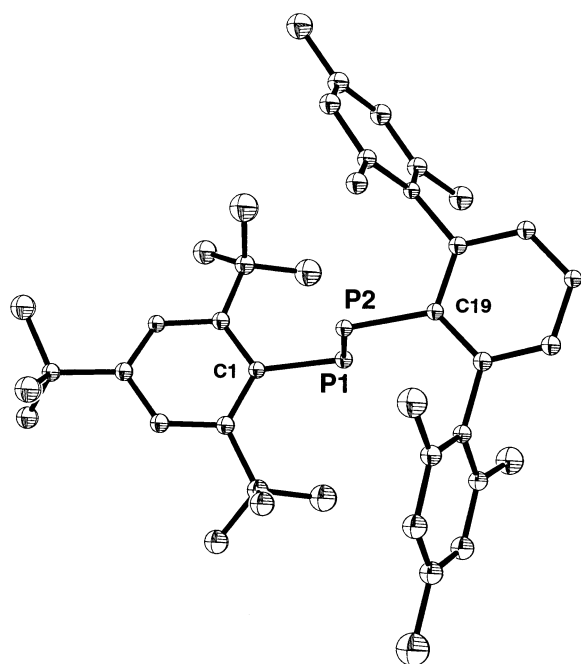
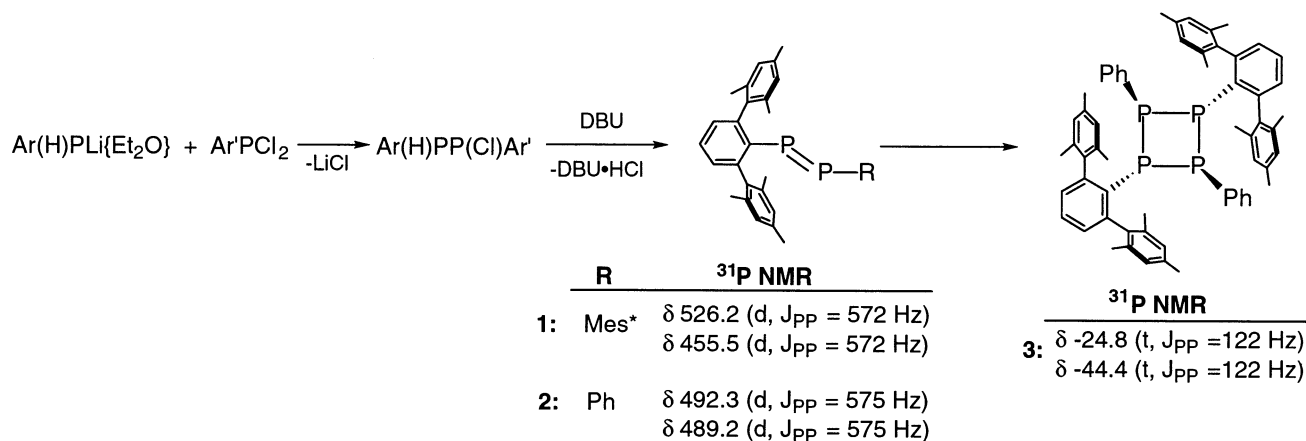
Diphosphene **1** is quite thermally robust and was fully characterized. Deep yellow crystals of **1** suitable for X-ray diffraction studies were grown from an ether–hexanes

(6) Urnezius, E.; Protasiewicz, J. D. *Main Group Chem.* **1996**, *1*, 369.  
(7) Cowley, A. H.; Norman, N. C.; Pakulski, M. In *Inorganic Syntheses*; Ginsberg, A. P., Ed.; McGraw-Hill: New York, 1990; Vol. 27, p 235.

(8) Shah, S.; Simpson, M. C.; Smith, R. C.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **2001**, *123*, 6925.

(9) Tsuji, K.; Sasaki, S.; Yoshifuji, M. *Tetrahedron Lett.* **1999**, *40*, 3203.

Scheme 1



**Figure 1.** Structure of DmpP=PMes\* (**1**).

mixture at  $-35\text{ }^{\circ}\text{C}$ . The results of a structure determination are presented in Figure 1. Selected bond lengths and angles are presented in Table 2. The primary feature of interest, the P=P bond length of 2.024(13) Å, is within the range of reported P=P bond lengths (1.985–2.049 Å) for diphosphenes.<sup>2,6</sup> Structures of asymmetric diphosphenes are somewhat scarce by comparison to symmetric diphosphenes. Another interesting aspect of this structure is that it allows for structural comparisons between the two comparably sized sterically encumbered ligands Mes\* and Dmp about a multiply bonded unit.<sup>10</sup> Comparisons can also be drawn to the two symmetric analogues DmpP=PDmp<sup>6</sup> and Mes\*P=PMes\*,<sup>1</sup> which display P=P bond lengths of 1.985(2) and 2.034(2) Å, respectively. Angles about the phosphorus atoms in DmpP=PMes\* are 98.0(1) and 101.2(1) $^{\circ}$ . The larger PPC bond angle for the phosphorus atom bearing the Dmp group

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for **1** and **3**

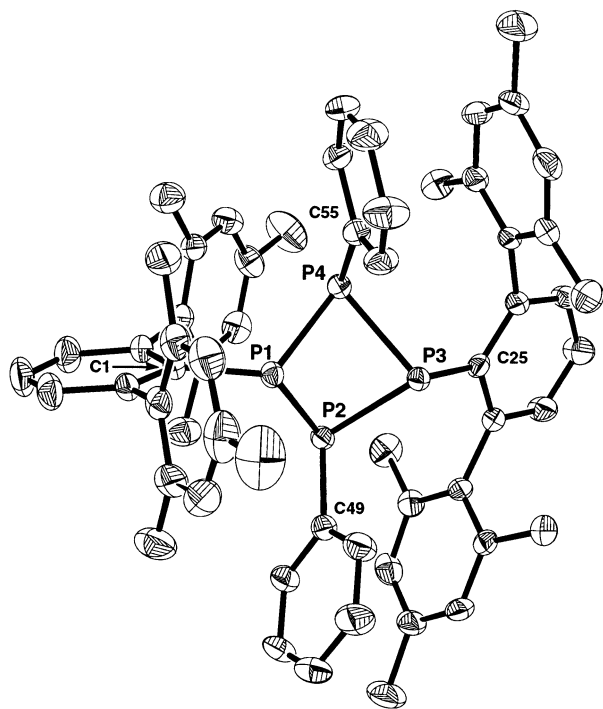
Compound <b>1</b>			
P(1)–P(2)	2.0240(13)	P(2)–C(19)	1.846(3)
P(1)–C(1)	1.860(3)		
C(1)–P(1)–P(2)	97.99(11)	C(6)–C(1)–P(1)	120.4(2)
C(19)–P(2)–P(1)	101.19(11)	C(20)–C(19)–P(2)	118.1(2)
C(2)–C(1)–P(1)	120.4(3)	C(24)–C(19)–P(2)	121.7(3)
Compound <b>3</b>			
P(1)P–(2)	2.228(2)	P(1)–C(1)	1.838(6)
P(1)–P(4)	2.233(2)	P(2)–C(49)	1.852(6)
P(2)–P(3)	2.242(2)	P(3)–C(25)	1.855(6)
P(3)–P(4)	2.252(2)	P(4)–C(55)	1.842(6)
P(2)–P(1)–P(4)	82.84(7)	C(55)–P(4)–P(1)	97.1(2)
P(1)–P(2)–P(3)	78.33(7)	C(55)–P(4)–P(3)	105.1(2)
P(2)–P(3)–P(4)	82.07(7)	C(30)–C(25)–P(3)	121.8(4)
P(1)–P(4)–P(3)	78.02(7)	C(26)–C(25)–P(3)	118.8(4)
C(1)–P(1)–P(2)	109.0(2)	C(54)–C(49)–P(2)	116.5(5)
C(1)–P(1)–P(4)	114.9(2)	C(50)–C(49)–P(2)	125.2(5)
C(49)–P(2)–P(1)	98.7(2)	C(2)–C(1)–P(1)	128.9(5)
C(49)–P(2)–P(3)	105.7(2)	C(6)–C(1)–P(1)	112.5(4)
C(25)–P(3)–P(2)	107.65(19)	C(60)–C(55)–P(4)	125.2(5)
C(25)–P(3)–P(4)	107.44(18)	C(56)–C(55)–P(4)	116.2(5)

might suggest that this group is effectively more bulky than the Mes\*, but the PC bond lengths are in contradiction to this simple view. In addition, it appears that an atom bearing a single hindered aryl is better shielded by a Mes\* group, while an atom bearing two aryls is more crowded having two terphenyl groups.<sup>11</sup> The PPC bond angles in **1** are within the range of corresponding values observed in DmpP=PDmp (109.8(1) and 97.4(3) $^{\circ}$ ) and Mes\*P=PMes\* (102.8(1) $^{\circ}$ ). The P=P unit in **1** is deflected completely out of the plane of each attached aromatic ring (ca. 87 $^{\circ}$ ), due to the massive sizes of the sterically encumbered groups. By contrast, the P=P functional group in DmpP=PDmp is deflected away from the plane of only one of the two attached aromatic rings (81 $^{\circ}$ ) and only marginally so for the other (13 $^{\circ}$ ). In Mes\*P=PMes\*, the P=P group is displaced by a more modest degree (62 $^{\circ}$ ). As noted previously, interactions across the E=E array may also play a significant role in dictating the orientation of EE units in *meta*-terphenyl-substituted multiply bonded systems.<sup>12,13</sup>

(10) For an example of both Dmp and Mes\* groups about a structurally characterized Be–S singly bonded group, see: Niemeyer, M.; Power, P. P. *Inorg. Chem.* **1997**, *36*, 4688.

(11) Wehmschulte, R. J.; Grigsby, W. J.; Schiemenz, B.; Bartlett, R. A.; Power, P. P. *Inorg. Chem.* **1996**, *35*, 6694.

(12) Twamley, B.; Sofield, C. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1999**, *121*, 3357.

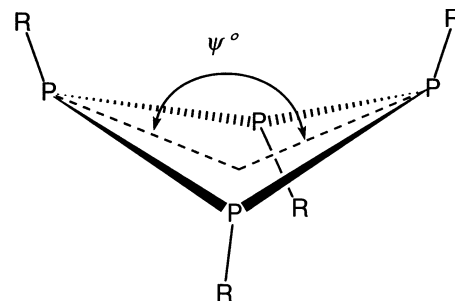


**Figure 2.** Structure of  $[\text{DmpPPPPh}]_2$  (**3**).

Diphosphene **2**, in contrast to **1**, rapidly undergoes dimerization in solution to the cyclotetraphosphane  $[\text{DmpPPPPh}]_2$  (**3**, Scheme 1) in high yield.  $^{31}\text{P}$  NMR coupling constants and multiplicity for **3** indicate that the  $\text{P}_4$  ring has its substituents arranged as portrayed in Scheme 1. Such an arrangement presumably allows the massive Dmp groups to be maximally disposed about the  $\text{P}_4$  ring.

This spatial arrangement was further confirmed by analysis of a single crystal of **3** by X-ray diffraction (Figure 2). Each phosphorus atom that comprises the  $\text{P}_4$  ring is pyramidal, with a slightly greater distortion toward planarity for the phosphorus atoms bearing the larger Dmp groups ( $\Sigma_{\text{B.A.}}(\text{P1}) = 307^\circ$ ,  $\Sigma_{\text{B.A.}}(\text{P3}) = 297^\circ$ ), compared to phosphorus atoms carrying Ph groups ( $\Sigma_{\text{B.A.}}(\text{P2}) = 283^\circ$ ,  $\Sigma_{\text{B.A.}}(\text{P4}) = 280^\circ$ ). The arrangement of the two Dmp groups is such that the two massive units are nearly orthogonal to one another, most likely in response to steric interactions between the two units. The Dmp unit attached to P3 is near enough to the two phenyl rings on P1 and P2 to suggest potential  $\pi$ -stacking interactions with its two mesityl rings, as indicated by centroid–centroid distances of 3.79 and 3.82 Å.<sup>14</sup> The P–P bond lengths around the ring range from 2.228 to 2.252 Å and are consistent with phosphorus–phosphorus single-bond lengths found for other  $(\text{RP})_4$  rings.<sup>15</sup>

The  $\text{P}_4$  ring in **3** is clearly nonplanar and the puckering is fairly significant. The puckering in  $\text{P}_4$  rings is usually described by a folding angle  $\psi$  (Figure 3).<sup>16</sup> Values of  $\psi$



**Figure 3.** Fold Angle  $\psi$ .

span a wide range, from nearly planar value of  $173.1^\circ$  for  $[\text{BuC}(\text{O})\text{P}]_4$ <sup>17</sup> to highly open values of 110.0 and  $113.6^\circ$  experimentally determined for  $[(\text{Me}_3\text{Si})_2\text{CHP}]_4$ <sup>18</sup> and  $[(\text{Me}_3\text{Si})_2\text{NP}]_4$ ,<sup>19</sup> respectively. The corresponding two values (due to asymmetry of the molecule) of 113.9 and  $116.2^\circ$  for **3** is at the open end of the spectrum of folding angles for this class of compounds. The asymmetry of **3** and overall structure are closely paralleled in the structure of  $[\text{TmpPPPPh}]_4$  (Tmp = 2,2,6,6-tetramethylpiperidyl)<sup>19</sup> ( $\psi = 115.4$  and  $119.3^\circ$ ). For example, the closest contacts between opposite pairs of phosphorus atoms across the rings of **3** are 2.824 and 2.951 Å, close to corresponding values of 2.803 and 3.061 Å for  $[\text{TmpPPPPh}]_4$ .

Diphosphenes similar to **1** and **2** ( $[\text{DmpP}=\text{PR}]$ ) having R groups between the sizes of Mes\* and Ph ( $\text{R} = \text{tBu}$  or  $\text{Ar}' = 2,6\text{-}(4\text{-tBuC}_6\text{H}_4)_2\text{C}_6\text{H}_3$ ) were generated by the synthetic route used for **1**.<sup>20</sup> These diphosphenes, like **2**, underwent further reaction in solution and appear to yield mixtures of cyclotetraphosphanes (as suggested by  $^{31}\text{P}$  NMR spectroscopy), but these mixtures were more difficult to fully characterize.

## Conclusions

Two new diphosphenes were prepared and fully characterized. The first,  $\text{DmpP}=\text{PMes}^*$  (**1**), is an interesting diphosphene that carries two different types of sterically demanding ligands. The second,  $\text{DmpP}=\text{PPh}$ , is unstable and rapidly dimerizes to the cyclotetraphosphane  $[\text{DmpPPPPh}]_2$  (**3**). Both **1** and **3** have been structurally characterized by single-crystal X-ray diffraction.

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

**Supporting Information Available:** Crystallographic files in CIF format. This information is available free of charge via the Internet at <http://www.acs.org>.

IC025759L

- (13) Phillips, A. D.; Wright, R. J.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2002**, *124*, 5930.  
 (14) (a) Dahl, T. *Acta Chem. Scand.* **1994**, *48*, 95. (b) Hobza, P.; Selzle, H. L.; Schlag, E. W. *Chem. Rev.* **1994**, *94*, 1767. (c) Hunter, C. A. *Chem. Soc. Rev.* **1994**, 101. (d) Chipot, C.; Jaffe, R.; Maigret, B.; Pearlman, D. A.; Kollman, P. A. *J. Am. Chem. Soc.* **1996**, *118*, 11217. (e) Sun, S.; Bernstein, E. R. *J. Phys. Chem.* **1996**, *100*, 13348.

- (15) (a) Baudler, M.; Glinka, K. *Chem. Rev.* **1993**, *93*, 1623. (b) Cowley, A. H.; Pinnell, R. P. In *Topics in Phosphorus Chemistry*; Gragson, M., Griffith, E. J., Eds.; New York, 1967; Vol. 4, p 1.  
 (16) Schoeller, W. W.; Busch, T. *Chem. Ber.* **1991**, *124*, 1369–1371.  
 (17) Knock, F.; Appel, R.; Barth, V. Z. *Kristallogr.* **1996**, *211*, 343.  
 (18) Schmitz, M.; Leininger, S.; Bergsträsser, U.; Regitz, M. *Heteroatom Chem.* **1998**, *9*, 453–460.  
 (19) Appel, R.; Gudat, D.; Niecke, E.; Nieger, M.; Porz, C.; Westermann, H. Z. *Naturforsch.* **1991**, *46b*, 865.  
 (20)  $^{31}\text{P}$  NMR data:  $\text{DmpP}=\text{P}^i\text{Bu}$ ,  $\delta$  567.0, 482.7 (d,  $J_{\text{PP}} = 574$ );  $\text{DmpP}=\text{PAr}'$ ,  $\delta$  526.2, 497.1 (d,  $J_{\text{PP}} = 575$ ).