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A closer look at the phosphorus–phosphorus double bond lengths in *meta*-terphenyl substituted diphosphenes

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Dedicated to Arnold L. Rheingold

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ABSTRACT

The single crystal X-ray structure of DmpP=PDmp (**1**, Dmp = 2,6-$Mes_2C_6H_3$), which was previously reported to have a relatively short P=P bond distance of 1.985(2) Å at room temperature, has been reexamined at variable temperatures. Crystallographic analyses of **1** at 100 K allow for resolution of disorder of the two phosphorus atoms (which is unresolvable from room temperature diffraction data), and for determination of a more conventional P=P bond length of 2.029(1) Å. Single crystals of the closely related diphosphene DxpP=PDxp (**2**, Dxp = 2,6-(2,6-$Me_2C_6H_3)_2C_6H_3$) show similar disorder in one of two crystallographically independent molecules in the unit cell. A value of 2.0276(4) Å is found for the non-disordered P=P bonds at 100 K for **2**. A new diphosphene Ar′P=PAr′ (**3**, Ar′ = 2,6-Mes_2-4-OMe–C_6H_3) has been prepared and its structure has also been examined. The P=P bond length for **3** was determined to be 2.0326(9) Å and relatively free of the effects of disorder.

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1. Introduction

> "This all comes back to my long-held observation that I have never met a competent crystallographer that wasn't also a first-rate chemist."
>
> -Professor Arnold Rheingold, 1-21-2010, commenting on the Bruker User List for the need for reviewers who have competency in both of these areas.

Professor Rheingold has been an active advocate for more chemists to become competent crystallographers, and for crystallographers to make sure the structures they produce are chemically reasonable. Chemists working on compounds having multiple bonds between main group elements are often fixated upon bond distances obtained from crystallographic studies. In particular, a shorter bond can be an important indicator of multiple bonding. For the heavier elements, however, the decrease in bond lengths with increased bond order is much less dramatic than witnessed for carbon–carbon or nitrogen–nitrogen bonds [1]. There is thus need for extra care in examining such distances.

One of the earlier Group 15 elements to illustrate bond length shortening upon double bond formation is the first structurally characterized diphosphene $Mes^*P{=}PMes^*$ by Yoshifuji in 1981 (Mes^* = 2,4,6-$^tBu_3C_6H_2$) [2]. This landmark compound was found to have a phosphorus–phosphorus bond length of 2.034(2) Å at room temperature, representing a 8.4% reduction of bond length from the average value of 2.22 Å for a PP single bond. A later determination of this structure by Cowley at 100 K, and with a larger data set, yielded a value of 2.047(1) Å (0.17 Å, 7.8% reduction from PP single bond average) [3]. While these contractions may not be as great as for compounds having analogous N=N linkages, they still argue for the presence of significant π-bonding between the phosphorus atoms.

Our group reported the structure of the diphosphene DmpP=PDmp bearing a sterically encumbered *meta*-terphenyl ligand Dmp (Dmp = 2,6-$Mes_2C_6H_3$) [4]. A key metric determined from this study was the P=P bond length of 1.985(2) Å (0.23 Å shorter, or a 10.6% reduction, from PP single bond value). This bond length is the shortest reported to date for two coordinate phosphorus atoms in acyclic RP=PR molecules. Even allowing for three sigma units in standard deviation leads to a maximum bond length of 1.991 Å, a value that still lies shorter than those for most other diphosphenes. Our continuing interest in these types of molecules and recently upgraded diffraction facilities allowed us to reexamine this material. Here we report on the results of new diffraction experiments on **1** and two closely related derivatives. In particular, the temperature dependence of the crystallography findings offer important insights as to the interpretation of the short P=P bond length originally reported for **1** and similar systems. Comparisons are also drawn to structurally characterized *meta*-terphenyl sheltered diphosphenes **4**–**7** (Chart 1) showing P=P distances ranging from 2.008(2) to 2.039(2) Å [5–8].

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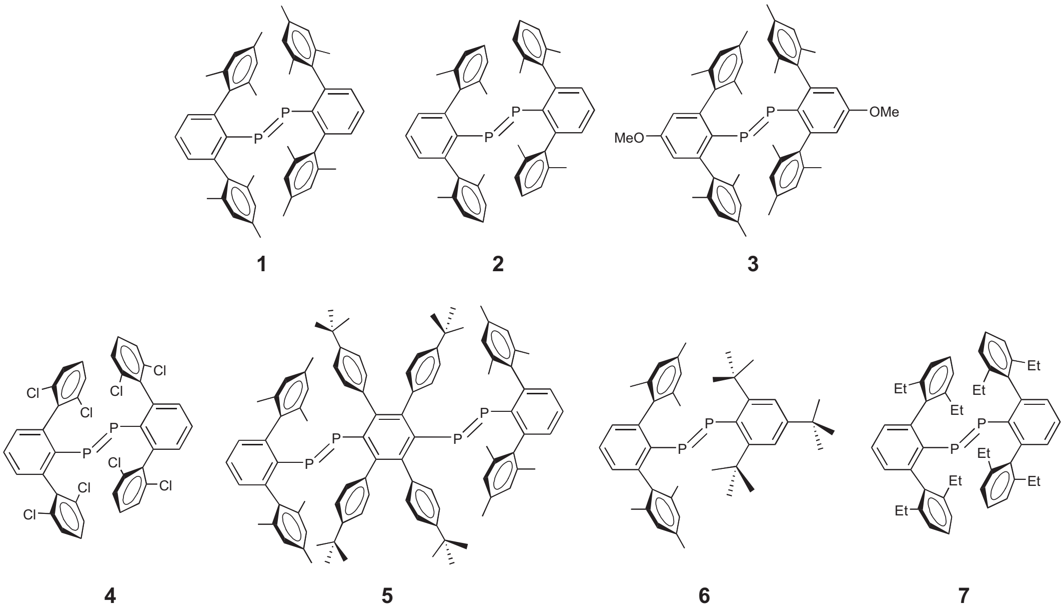

Chart 1.

2. Results and discussion

2.1. Structure analyses of DmpP=PDmp

Five new crystals of compound **1**, grown from pentane at −35 °C in a drybox, were examined at a variety of temperatures. Two samples were examined independently at 100 K, a third at 190 K and at 290 K, a fourth at 300 K, and a fifth sample was measured at 300 K, 200 K, and at 100 K. As the overall results for all 5 samples are consistent with one another ($P2_1/c$, similar cells, R_1 values spanning from 3–6%), only data for the fifth sample will be presented and discussed. The orange crystal of **1** was mounted on a glass fiber with epoxy and subjected to crystallographic analyses at 300 K, 200 K, and 100 K. Relevant data collection and solution details are provided in Tables 1 and 2.

From 300 K to 100 K the cell volume shows a 4.1% decrease, dominated by decreases in the *a* and *c* axis lengths (2.3% and 1.7%, respectively) and the change in the β angle (0.71%). The *b* axis shows little change (0.12%). The 300 K data set yields a structural solution (solution 1*B*′) comparable to the reported RT structure of **1**, in that commonly acceptable *R*-factors and Goodness-of-fit are produced, and a "short" P=P bond length of 1.9893(9) Å is realized. Three views of thermal ellipsoid diagrams for the inner core atoms of **1** are presented in Fig. 1. While the thermal ellipsoids for the phosphorus atoms appear normal to the casual observer, submission of the Cif file for 1*B*′ to Check Cif [9] generates a Level B warning for the Hirshfeld rigid bond test [10] difference for P1–P2 (11.25 su). This test notes significant differences in anisotropic thermal parameters along chemical bonds and can be an indicator of disorder, among other things. The largest difference peaks in the residual electron density map occur near P1 and P2 (0.79 and 0.56), and one can introduce a disorder model of the type depicted in Chart 2.

This approach reduces the final *R*-factors and residual peaks in the difference map to give solution 1*B*″. The resulting pair of P=P bond distances of 1.999(5) and 1.975(8) Å for the 53/47 model of the disorder, however, remain below that of typical disphosphene bond lengths. Furthermore, the thermal parameters for the second set of phosphorus atoms are larger and less isotropic than for the

Table 1
Important variable temperature diffraction information for compound **1**.

Solution-data set	1B	1C	1D
Empirical formula	$C_{48}H_{50}P_2$	$C_{48}H_{50}P_2$	$C_{48}H_{50}P_2$
Formula weight	688.82	688.82	688.82
Temperature (K)	300	200	100
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions			
a (Å)	10.9346 (1)	10.7974 (1)	10.6802 (1)
b (Å)	22.2979 (3)	22.2807 (2)	22.2695 (3)
c (Å)	16.9984 (2)	16.8506 (2)	16.7013 (2)
α (°)	90.00	90.00	90.00
β (°)	91.048 (1)	90.756 (1)	90.404 (1)
γ (°)	90.00	90.00	90.00
V (Å^3)	4143.83 (8)	4053.46 (7)	3972.18 (8)
Z	4	4	4
D_{calc} (g cm^{-3})	1.104	1.129	1.152
Absorption coefficient (mm^{-1})	0.14	0.14	0.14
F(0 0 0)	1472	1472	1472
Crystal size (mm)	0.35 × 0.30 × 0.20	0.35 × 0.30 × 0.20	0.35 × 0.30 × 0.20
Crystal color and shape	pale orange block	pale orange block	pale orange block
θ Range data collection	1.51–28.3	1.52–28.3	1.52–28.3
Limiting indices	$-14 < h < < 14$ $-29 < k < 29$ $-22 < l < 22$	$-14 < h < 14$ $-29 < k < 29$ $-22 < l < 22$	$-14 < h < 14$ $-29 < k < 29$ $-22 < l < 22$
Completeness (%)	99.9	99.9	99.9
Reflections collected	52 637	51 361	50 220
Independent reflections $R_{(int)}$	10317 (0.034)	10074 (0.030)	9876 (0.027)

Table 2
Key refinement and structural results for compound **1**.

Refinement method	Full-matrix least-square on F^2					
Solution	1*B*′	1*B*″ w/disorder [occupancy]	1*C*′	1*C*″ w/disorder [occupancy]	1*D*′	1*D*″ w/disorder [occupancy]
Temperature (K)	300	300	200	200	100	100
Data/restraints/parameters	10 317/0/463	10 317/0/482	10 074/0/463	10 074/0/482	9876/0/463	9876/0/482
Goodness-of-fit (GOF) on F^2	1.05	1.01	1.04	1.04	1.02	1.03
Final *R* indices [$I > 2\sigma(I)$]^{a,b}	$R_1 = 0.0588$ $wR_2 = 0.155$	$R_1 = 0.0479$ $wR_2 = 0.125$	$R_1 = 0.0526$ $wR_2 = 0.134$	$R_1 = 0.0427$ $wR_2 = 0.110$	$R_1 = 0.0434$ $wR_2 = 0.110$	$R_1 = 0.0371$ $wR_2 = 0.0913$
R indices (all data)	$R_1 = 0.1051$ $wR_2 = 0.183$	$R_1 = 0.0925$ $wR_2 = 0.149$	$R_1 = 0.0748$ $wR_2 = 0.150$	$R_1 = 0.0641$ $wR_2 = 0.122$	$R_1 = 0.0546$ $wR_2 = 0.117$	$R_1 = 0.0482$ $wR_2 = 0.0980$
$d_{P=P}$ (Å)	1.9893(9)	1.999(5) [53] 1.975(8) [47]	2.0098(7)	2.018(1) [90] 2.056(1) [10]	2.0263(5)	2.029(1) [78] 2.009(9) [22]
Highest residual peak	0.79	0.24	0.96	0.29	1.29	0.35

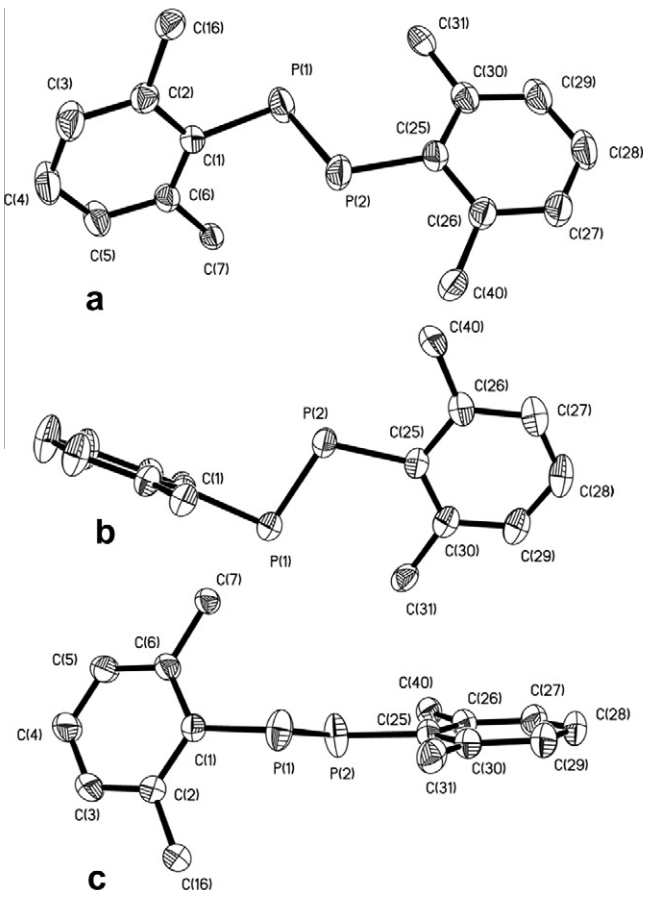

Fig. 1. Three thermal ellipsoid plots (30% probability) of 300 K solution (1*B*′) of **1** for selected atoms. Hydrogen atoms, and all but ipso carbon atoms of mesityl groups, omitted for clarity.

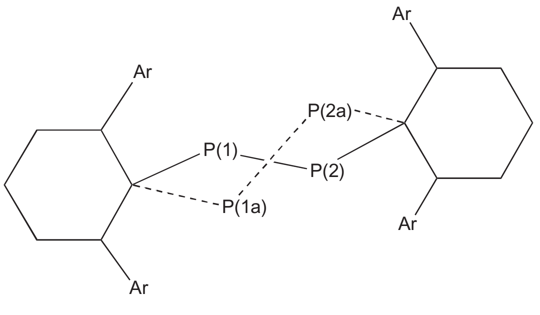

Chart 2.

first set. While introduction of the restraints DELU and/or SIMU produces slight changes in the final data for this structure, no significant impact on the P═P bond lengths are realized and thus these restraints were not used (similar results for use of SIMU/DELU on solution 1*B*′ were found).

While the disorder model for the 300 K structure provides better statistics, it does not address the key question of the anomalously short P═P bond length in **1**, and may be of questionable crystallographic rigour. When unusually short bond distances have been determined unrelated to disorder, libration effects have been invoked. Libration, or large scale oscillation about bonds, can yield reduced bond length findings. These effects tend to be most important for lighter atoms and for structures performed at room temperature. Using the LIBR option in XP [11], an estimated impact of 0.003 Å (a P═P length of 1.993 Å) was found for the structure of **1**.

The crystal was cooled to 200 K and data collected using otherwise identical conditions (**1C**). The solution of the structure without (1*C*′) and with a disorder model (*1C*″) led to the data in Tables 1 and 2. The results mirror that obtained for the 300 K structure, but with some subtle differences. First, the P═P distances have increased slightly, and are closer to the range of other structurally determined P═P distances. Second, the solution having the disorder model (1*C*″) changed from 53/47 to 90/10 fit. This fact suggests that the disorder within crystals **1** might be dynamic, and temperature dependent.

The crystal of **1** was further cooled to 100 K, and a third data set (**1D**) was collected under identical conditions. The corresponding structural solutions without (1*D*′) and with (1*D*″) the disorder model yielded results that are shown in Tables 1 and 2 as well. The resulting P═P bond lengths have increased further, and are only slightly shorter than those values of the aforementioned Mes*P═PMes* molecule. Oddly, as opposed to solution 1*B*″ and 1*C*″, solution 1*D*″ refined to yield a 78/22 occupancies for the disordered phosphorus atoms. The fluctuations in occupancies among the three temperatures might reflect a shallow potential surface or an unknown artifact.

As compared to the previously published structure of **1**, the "best" solution seems to be 1*D*″, and 2.029(1) Å should be taken as the best value of the P═P bond length as it is based on the molecule having the highest occupancy (and more certainty). The value for the minor component (P1A and P2A) not only contains greater error (2.009(9) Å), but the Check Cif report indicates remaining issues for the thermal parameters for P1A and P2A (large $U_{eq(max)}/U_{eq(min)}$ range). Attempts to squeeze finer details from P1A and P2A and remove this warning were unsuccessful. It is also important to note that while the second set of phosphorus atoms are not far displaced from the first (0.13 and 0.25 Å), notable changes in PP distances occur upon these slight displacements. Regardless, this structure provides another reminder of the importance of low temperatures for optimal X-ray structural solutions [12].

2.2. Structure analysis of DxpP=PDxp (**2**)

Preliminary diffraction studies of **2** were mentioned in a previous report [4]. Relatively poor crystal quality and disorder issues, however, hampered successful refinement at that time. Armed with better knowledge of the disorder in crystals of **1** and better equipment, this structure was again investigated. Single crystals of **2** were thus examined at 100 K and 200 K and the results of X-ray determinations presented in Tables 3 and 4. Interestingly, the structure of **2** contains two independent molecules in the asymmetric unit, only one of which possesses the disorder displayed by compound **1**.

Table 3
Important diffraction information for compounds **2** and **3**.

Solution-data set	**2A**	**2B**	**3**
Empirical formula	$C_{44}H_{42}P_2$	$C_{44}H_{42}P_2$	$C_{50}H_{54}O_2P_2$
Formula weight	632.72	632.72	748.87
Temperature (K)	200	100	100
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Unit cell dimensions			
a (Å)	11.2740 (2)	11.2056 (2)	2.2796 (6)
b (Å)	17.7924 (3)	17.6872 (2)	19.458 (1)
c (Å)	19.5055 (4)	19.4574 (3)	18.382 (1)
α (°)	111.624 (1)	111.767 (1)	90.00
β (°)	92.352 (1)	92.666 (1)	103.062 (4)
γ (°)	91.101 (1)	91.053 (1)	90.00
V (Å^3)	3631.7 (3)	3574.90 (9)	4278.5 (4)
Z	4	4	4
D_{calc} (g cm^{-3})	1.157	1.176	1.163
Absorption coefficient (mm^{-1})	0.15	0.15	0.14
F(0 0 0)	1344	1344	1600
Crystal size (mm)	0.45 × 0.20 × 0.20	0.45 × 0.20 × 0.20	0.14 × 0.12 × 0.07
Crystal color and shape	orange block	orange block	orange plate
θ Range data collection	1.12–30.68	1.13–30.48	2.00–28.3
Limiting indices	$-16 < h < 16$ $-25 < k < 25$ $-28 < l < 27$	$-15 < h < 15$ $-25 < k < 25$ $-27 < l < 27$	$-16 < h < 14$ $-25 < k < 18$ $-24 < l < 24$
Completeness (%)	98.6	99.4	99.1
Reflections collected	104 715	102 423	38 306
Independent reflections (R_{int})	22 201 (0.0446)	21 626 (0.0358)	10 567 (0.0979)

The data obtained at 100 K can be refined successfully without disorder modeling (solution 2*B*′) to provide reasonable *R* factors and what might be acceptable PP bond lengths of 2.0276(5) and 2.0109(6) Å for each of the two independent molecules in the unit cell. Closer examination, however, shows that one of these two molecules showed behavior akin to that of **1** above. Introduction of the same type of disorder model gives solution 2*B*″ and revealed two sets of P=P atoms in a 87:13 ratio. The resulting P=P bond lengths of 2.009(1) and 2.006(1) Å, however, have greater error and differ somewhat from the value of 2.0276(4) for the P=P bond in the second non-disordered molecule. Fig. 2 shows the resulting diagrams for this refinement.

At 200 K the results are less satisfactory. Without disorder modeling (solution 2*A*′), the P=P distances were found to be 2.0176(8)

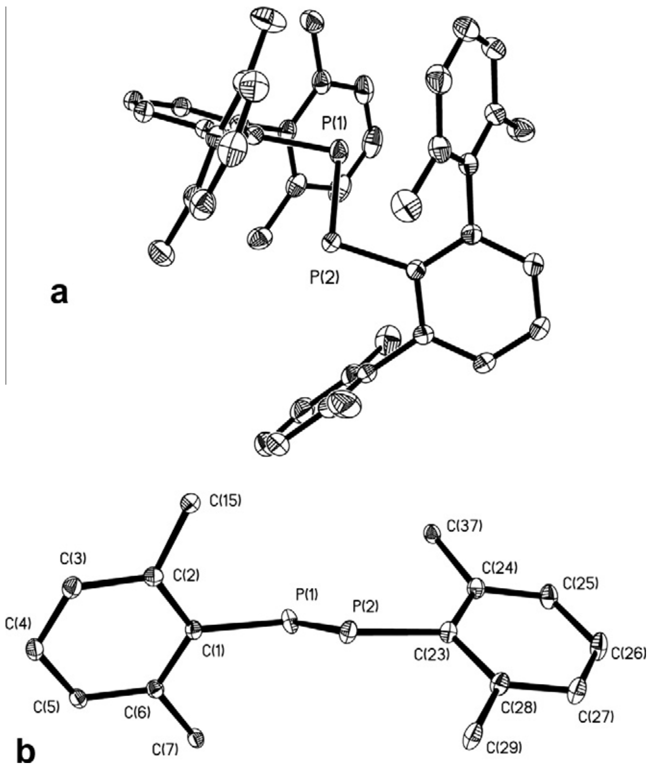

Fig. 2. Two thermal ellipsoid plots (50% probability) of 100 K solution (**2***B*″) of non-disordered molecule of **2**. The second independent molecule in cell not shown. (**a**) All non-hydrogen atoms (**b**) hydrogen atoms and all but ipso carbon atoms of xylyl groups, omitted for clarity.

Table 4
Key Refinement and Structural Solution Results for **2** and **3**.

Refinement method	Full-matrix least-square on F^2				
Solution	2*A*′	2*A*″ w/disorder (occupancy)	2*B*′	2*B*″ w/disorder (occupancy)	**3**
Temperature (K)	200	200	100	100	100
Data/restraints/parameters	22 201/0/846	22 201/0/864	21 626/0/845	21 626/0/864	10 567/0/501
Goodness-of-fit (GOF) on F^2	1.04	1.02	1.03	1.03	1.01
Final R indices $[I > 2\sigma(I)]^{a,b}$	$R_1 = 0.0685$ $wR_2 = 0.173$	$R_1 = 0.0505$ $wR_2 = 0.126$	$R_1 = 0.0490$ $wR_2 = 0.124$	$R_1 = 0.0438$ $wR_2 = 0.111$	$R_1 = 0.0596$ $wR_2 = 0.133$
R indices (all data)	$R_1 = 0.1070$ $wR_2 = 0.200$	$R_1 = 0.0875$ $wR_2 = 0.147$	$R_1 = 0.0648$ $wR_2 = 0.135$	$R_1 = 0.0595$ $wR_2 = 0.122$	$R_1 = 0.1279$ $wR_2 = 0.170$
$d_{P=P}$ (Å)	2.0176(8), 1.975(1)	2.0173(6)/1.991(3)*/1.979(6)* [67/33]	2.0276(5), 2.0109(6)	2.0276(4), 2.009(1)*, 2.006(1)* [87/13]	2.0326(9)
Highest residual peak	2.19	0.31	1.8	0.50	0.75

* Disordered PP bonds of other molecule in cell.

and 1.975(1) Å. Introduction of the disorder model (2*A*″) for one of the two independent molecules in the cell resulted in P=P distances of 1.991(3) and 1.979(6) Å, and a P=P distance of 2.0173(6) Å for the non-disordered second molecule. Introduction of the restraints SIMU and/or DELU made little difference, and still yielded P=P distances below 2 Å.

The presence of two independent molecules in the unit cell of **2** provides a unique internal calibration for evaluating the success of these refinements. As the P=P bond distances from the disordered molecule in **2** seem "short" and contain greater error, it seems most appropriate to accept the value of 2.0276(4) Å as the best value for the P=P bond length in compound **2**, taken from only the non-disordered molecule from the refinement 2*B*″. This value agrees well with that determined for compound **1**.

2.3. Structure analysis of Ar′P=PAr′ (3)

Single crystals of **3** were subjected to X-ray diffraction analysis at 100 K and the results are presented in Tables 3 and 4. The molecule crystallizes in the *P*2(1)/*n* with one molecule in the asymmetric unit. Unlike the crystallography of **1** and **2**, attempts to find and refine a structural solution with the same type of disorder model were unsuccessful. The best unsuccessful attempt suggested at most a 6% contamination by a second set of phosphorus atoms could be estimated. Further, the solution without disorder modeling provides a P=P bond length of 2.0326(9) Å that is reasonable and falls into the expected range for such values. As such, it appears that this structure is reliable and the results are not clouded by disorder issues. Fig. 3 provides two views of the solution.

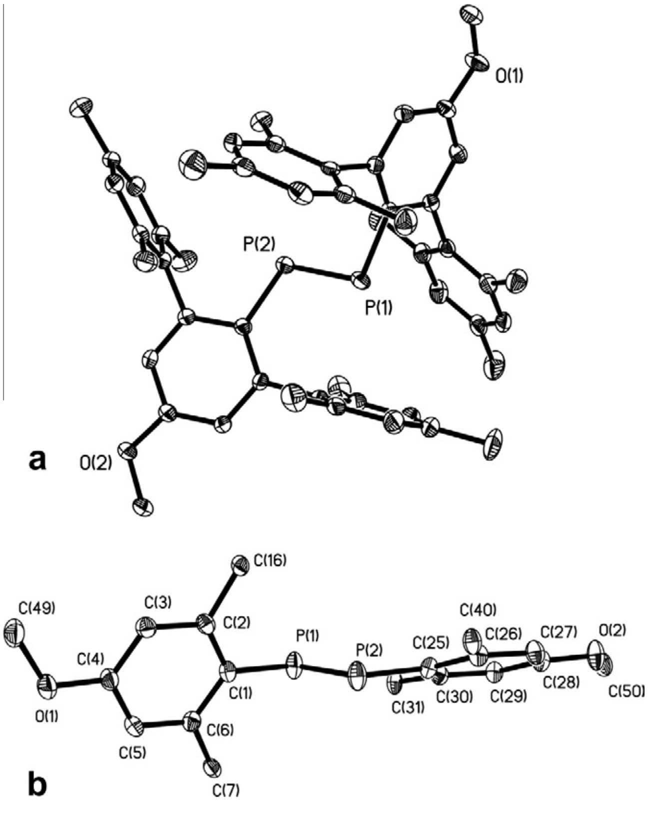

Fig. 3. Two thermal ellipsoid plots (50% probability) of 100 K solution of **3**. (**a**) All non-hydrogen atoms. (**b**) Hydrogen atoms and all but ipso carbon atoms of mesityl groups, omitted for clarity

2.4. Comparison to other meta-terphenyl sheltered diphosphenes, and predicted structures

Selected data for *meta*-terphenyl diphosphenes **1**–**7** (Chart 1) that have been structurally characterized are summarized in Table 5. The P=P bond lengths fall between 2.008(2)–2.039(2) Å. The most significant differences among **1**–**7** lie in the range of C–P–P bond angles. Values range from 95° to 109°. Additionally, the PPCC torsion angles vary greatly, with molecules like **1** and **7** having one aromatic ring nearly coplanar with P=P unit and the other ring nearly orthogonal, while other compounds have either a mix of angles or both rings nearly orthogonal. While packing forces likely play a role in the solid state structures of these materials, examination of the packing of these materials did not reveal any trends or evidence for significant π-stacking.

While computationally predicted structures for rather simple diphosphenes such HP=PH or PhP=PPh have been reported [13–15], few calculations have examined the undeniable role that the sterically encumbered ligands play upon structure. As the power of computational chemistry has grown over the recent years, the opportunity to tackle larger systems has become increasingly possible. For example, Tokitoh has reported on DFT (B3LYP) studies that predict P=P bond lengths of 2.088 and 2.068 Å for TbtP=PTbt and BbtP=PBbt, respectively (Tbt = 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl; Bbt = 2,6-bis[bis(trimethylsilyl)methl]phenyl) [16]. These values compare favorably with the corresponding experimentally determined values of 2.051(2) and 2.043(1) Å.

Similar calculations (B3LYP/3-21G(d)) have been performed on the full compound **1** (Fig. 4). A predicted P=P bond distance of 2.039 Å indeed compares well with the best experimental value of 2.029(1) Å for the major component of the disordered P=P unit of **1**. The C–P–P bond angles of 96.9 and 107.8° also agree well with those found experimentally (95.38(6) and 109.43(7)°).

2.5. Comparisons to stilbenes

Phosphorus is often called a "carbon copy" for its ability to provide analogs of compounds where multiply bonded carbon atoms are exchanged for the isolobal phosphorus containing equivalents [17]. Does the "carbon copy" concept span to the X-ray structural world? In fact, single crystal structures of stilbenes (and azobenzenes) can often show unusually short C=C bond lengths [18]. Most relevant to the structures of **1** and **2** are molecules such as *E*-2,2′-dimethylstilbene. The structure of this stilbene shows ethylenic CC distances that vary from 1.321(2) Å at 188 K to 1.283 (3) at 298 K [19–22]. A longer distance of 1.353 Å would be expected from MMP2 calculations. Unraveling the disorder that occurs in these systems is challenging, and in some cases, can not be discerned from X-ray structural data analyses alone. In addition, a dynamic motion in the crystalline state via a "pedal motion" is also present. Recent studies, performed at various temperatures and sometimes by shock cooling, have revealed that disorder/motion is likely present at all temperatures, even when low occupancy factors of minor conformers essentially make the disorder "invisible".

In the analysis of compound **1**, there was no evidence for these other types of disorder. The rather immense size of the *meta*-terphenyls used in the present study make movements of the large aryl groups in these diphosphene crystal less likely, but allow for displacements of attached atoms. The location of the phosphorus atoms in the crystalline ensemble give the (albeit not necessarily correct) impression that they can "rattle around" inside the protective cage provided by the sterically demanding ligands. Such disorder has often been observed [23]. In particular, the structure of DmpGe(Cl)Ge(Cl)Dmp exhibits nearly the same type of disorder described here for the germanium atoms [23b]. In addition, other types of crystallographic/chemical problems have been noted in

Table 5
Structural comparisons for diphosphenes bearing *meta*-terphenyl ligands.

Structure	$1D''$ [a]	$2B''$ [a]	**3**	**4** [b,c]	**5** [c]	**6**	**7**
Temperature (K)	100	100	100	233	300	173	173
$d_{P=P}$ (Å)	2.029(1)	2.0276(4)	2.0326(9)	2.039(2), 2.021(2)	2.008(2)	2.024(1)	2.017(2)
C–P–P angles (°)	95.38(6), 109.43(7)	98.33(4), 104.26(4)	97.62(8),109.32(8)	98.5(2), 98.1(2)	97.5 (2), 106.3(2)	101.2(1), 98.0(1)	98.0, 110.7
PPCC torsion angles	8.2, 75.0	63.0, 38.5	73.2, 21.1	88.7, 88.2	83.9, 30.1	82.5, 84.1	7.1, 76.3

[a] For best determined values (see text).
[b] Two independent molecules in asymmetric unit.
[c] Center of symmetry in molecule.

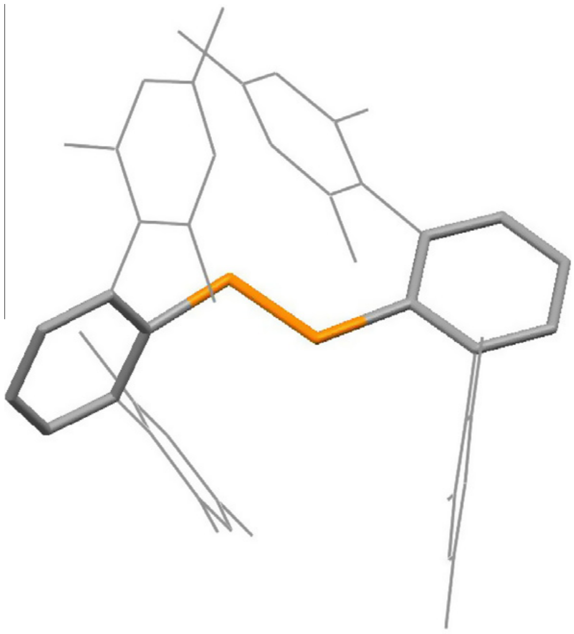

Fig. 4. Minimized structure of compound **1** (B3LYP/3-21G(d)), hydrogen atoms omitted for clarity.

meta-terphenyl main group compounds. For example, Power and colleagues has observed that while the diarsene DmpAs=AsDmp is not disordered (and exhibits a very different conformation than DmpP=PDmp), the distibene Ar″Sb=SbAr″ (Ar″ = 2,6-Trip$_2$C$_6$H$_3$) is plagued by cocrystallization with the partially reduced distibane Ar″Sb(Cl)Sb(Cl)Ar″ [24].

3. Conclusion

In summary, a reevaluation of the structure of compound **1** at several temperatures using diffraction data collected on a modern CCD-equipped diffractometer has been undertaken. The results indicate the presence of disorder that involves the phosphorus atoms. The resulting P=P bond lengths are influenced by the disorder, and are only of “conventional” values (i.e., fall into the range of previously determined P=P bond lengths) at low temperature. Thus, while the first structural report (room temperature) on **1** yielded a P=P distance of 1.985(2) Å, recent and better data at 300 K for **1** yield values of 1.999(5) and 1.975(8) Å with a disorder model in place, and 1.9893(9) Å without the disorder model. At 100 K, values of 2.029(1) and 2.010(9) Å are obtained with a disorder model in place, and 2.0263(5) Å without the disorder model. The values obtained at lower temperature for the major component (2.029(1) Å) are the best available for **1** should thus be used in describing the P=P bond length. Similar disorder exists in one of the two independent molecules of **2** in the crystal state, and again longer P=P bond lengths are determined at 100 K versus 200 K. The structure of **3**, determined at 100 K, features a P=P bond length of 2.0326(9) Å and no resolvable disorder of the phosphorus atoms. For reasons that are unclear, these systems are prone to yield erroneous P=P bond lengths and thus caution should be taken in structural analyses of *meta*-terphenyl substituted diphosphenes or other main group compounds.

4. Experimental

4.1. Materials

Compounds **1** and **2** were prepared as previously reported [4,25]. Compound **3** was prepared by reduction of the corresponding ArPCl$_2$ (Ar = 4-OMe-2,6-Mes$_2$–C$_6$H$_2$) [26] with magnesium metal as follows. In a 10 mL flask, 0.100 g (0.23 mmol) of 4-OMe-2,6-Mes$_2$–C$_6$H$_2$PCl$_2$ and 0.006 g (0.24 mmol) of magnesium metal was taken into 5 mL of dry THF under dinitrogen. The solution was subjected to ultrasound for 10 minutes to produce a dark orange colored solution. The flask was taken into a glove box and the solvent was removed under vacuum. The orange colored material was dissolved into 10 mL of pentanes and filtered through celite using a glass fritted funnel. The solvent was removed under vacuum leaving 0.053 g (66%) of compound **3** as a dark orange colored solid. ^{1}H NMR (CDCl$_3$): δ 6.71 (s, 8H), 6.49 (s, 4H), 3.71 (s, 6H), 2.30 (s, 12H), 1.67 (s, 24H). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 489.4.

4.2. Crystallography

Crystals of compounds **1** and **2** used for structural determinations were grown from concentrated pentane solutions of the corresponding compounds held at −35 °C. X-ray quality crystals of **3** were grown from a concentrated solution in diethyl ether at −35 °C. The X-ray intensity data were measured at varying temperatures (Oxford Cryostream 700) on a Bruker SMART Apex II CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (λ = 0.71073 Å) operated at 1500 W power. For samples that were analyzed only at 200 K and colder, crystals were frozen onto a MiTeGen micromount. Samples that were analyzed at higher temperatures were epoxied to glass fibers. The detector was placed at a distance of 6.00 cm from the crystal. Data were measured using omega scans of 0.5° per frame for 10 s. The frames were integrated with the Bruker SAINT© build in APEX II software package using a narrow-frame integration algorithm, which also corrects for the Lorentz and polarization effects. Absorption corrections were applied using AXScale. The structures were solved and refined using Bruker SHELXTL© (Version 6.14) software. Hydrogen atoms were introduced at idealized positions and refined as riding to attached carbon atoms.

4.3. Computations

All calculations employed the GAUSSIAN 03 [27] software package and were performed in parallel on Intel Pentium 4 Xeon EM64T quad-core processors. Kohn–Sham formalized density functional theory (DFT) was employed to calculate ground state structure with the B3LYP hybrid functional [28,29]. The global minima for **1** was fully structurally optimized at the B3LYP/3-21G(d) level of theory. Frequency calculations were performed finding all positive eigenvalues for the Hessian on the 3-21G(d) surface. The B3LYP/3-21G(d) level of theory have proven to rather accurate on larger systems like fullerenes [30].

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Appendix A. Supplementary material

CCDC 769606, 769607 and 769608 contain the supplementary crystallographic data for compounds **1**, **2** and **3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.07.018.

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