Stabilization of a Diphosphagermylene through pπ–pπ Interactions with a Trigonal-Planar Phosphorus Center**

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Abstract: *N-Heterocyclic carbenes and their heavier homologues are, in part, stabilized by delocalization of the N lone pairs into the vacant p-orbital at carbon (or a heavier Group 14 element center). These interactions are usually absent in the corresponding P-substituted species, owing to the large barrier to planarization of phosphorus. However, judicious selection of the substituents at phosphorus has enabled the synthesis of a diphosphagermylene, [(Dipp)₂P]₂Ge, in which one of the P centers is planar (Dipp = 2,6-diisopropylphenyl). The planar nature of this P center and the correspondingly short P−Ge distance suggest a significant degree of P−Ge multiple bond character that is due to delocalization of the phosphorus lone pair into the vacant p-orbital at germanium. DFT calculations support this proposition and NBO and AIM analyses are consistent with a Ge−P bond order greater than unity.*

Since the discovery of the first stable example in 1991, N-heterocyclic carbenes (NHCs) and their acyclic analogues have become indispensable, both as ligands for catalytically active transition-metal complexes and as organocatalysts themselves;[1,2] recent reports even suggest that NHC complexes of transition metals may exhibit anti-tumor activity.[3] The versatility of NHCs and related compounds is due to their unusually strong σ-donor (and correspondingly weak π-acceptor) properties and their remarkable stabilities. The latter may be attributed to: 1) the presence of electronegative nitrogen atoms directly adjacent to the carbene center, which stabilize the singlet over the triplet ground state; and 2) effective pπ–pπ interactions between the lone pairs on nitrogen and the vacant p-orbital at carbon, which substan-
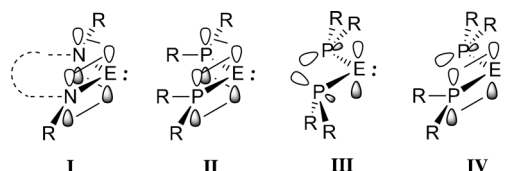
Scheme 1. Bonding situation in $(R_2N)_2E$: and $(R_2P)_2E$: species (E = Si, Ge, Sn, Pb).

tially mitigate the electron deficiency of this center (**I**, Scheme 1).

The corresponding heavier Group 14 analogues (diamidotetrylenes; $(R_2N)_2E$, E = Si, Ge, Sn, Pb) have a much longer history.[4] It is, perhaps, surprising then that the corresponding P-substituted species (diphosphatetrylenes; $(R_2P)_2E$)[5–7] and their carbene homologues (PHCs)[8] are rather less well established. This, at least in part, may be attributed to the high energetic barrier to achieving the optimum planar configuration at phosphorus that would enable efficient pπ–pπ overlap between the phosphorus lone pair and the vacant p-orbital on the adjacent Group 14 element center (**II**). In this regard, it is notable that the P atoms are distinctly pyramidal in all previously reported diphosphatetrylenes (**III**).[5,6]

However, calculations predict that the inherent π-donor capacity of phosphorus (that is, if the energy required for planarization is neglected) is almost identical to that of nitrogen.[9] Thus, if planarity could be induced at phosphorus, it should be possible to promote efficient pπ–pπ overlap in a diphosphatetrylene, stabilizing the electron-deficient Group 14 element center.

Few compounds with truly planar three-coordinate phosphorus centers have been reported.[10] However, it has been shown that the barrier to inversion (and therefore the barrier to planarization) at trigonal pyramidal phosphorus may be significantly reduced by: 1) the incorporation of the phosphorus center into a ring; 2) the use of bulky substituents; and 3) the presence of electropositive elements directly adjacent to phosphorus.[10,11] Strategies (1) and (2) were neatly applied by Bertrand and co-workers in the synthesis of the first P-heterocyclic carbene, in which the two phosphorus centers approach planarity (sum of angles at P = 353 and 348°).[8]

With the foregoing in mind, we posited that a sterically encumbered diphosphatetrylene, in which one of the phosphorus substituents is, necessarily, an electropositive center, would satisfy the conditions necessary for planarization at phosphorus and so provide the first example of a tetrylene stabilized by P−E pπ–pπ interactions.

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Treatment of PCl$_3$ with two equivalents of DippLi-(OEt$_2$),[12] followed by one equivalent of LiAlH$_4$ gave, after an aqueous work-up, the secondary phosphane (Dipp)$_2$PH (**1**) as a colorless, crystalline solid in good yield (Dipp = 2,6-iPr$_2$C$_6$H$_3$). The reaction between **1** and PhCH$_2$K in THF gave the potassium complex [(Dipp)$_2$P]K, which was reacted in situ with half an equivalent of GeCl$_2$(1,4-dioxane) to give a deep red solid, after removal of KCl and solvent (Scheme 1). Crystallization of this solid from cold toluene gave single crystals of the diphosphagermylene [(Dipp)$_2$P]$_2$Ge (**2**) as air-sensitive, dark red blocks suitable for X-ray crystallography in reasonable yield (Scheme 2).

Compound **2** crystallizes as discrete monomers with a V-shaped P$_2$Ge core and is, to the best of our knowledge, the first crystallographically characterized diphosphagermylene with a two-coordinate germanium center (Figure 1).[5,13] The
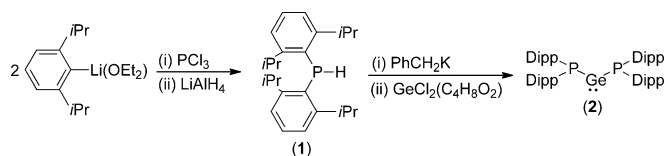
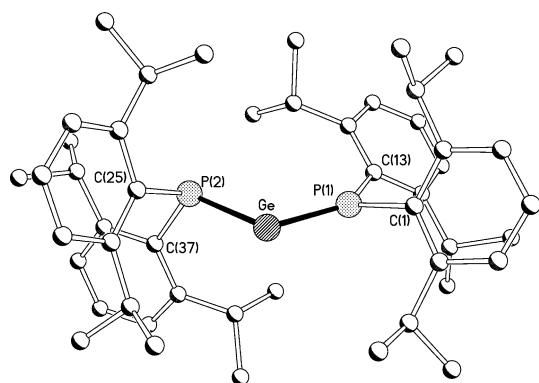**Scheme 2.** Synthesis of **2**. Dipp = 2,6-iPr$_2$C$_6$H$_3$.

Figure 1. Molecular structure of **2** with H atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge–P1 2.2337(11), Ge–P2 2.3823(12), P1–C1 1.839(4), P1–C13 1.846(4), P2–C25 1.866(4), P2–C37 1.851(4); P1-Ge-P2 107.40(4), C1-P1-Ge 108.33(14), C13-P1-Ge 144.33(15), C1-P1-C13 105.69(19), C25-P2-Ge 89.38(13), C37-P2-Ge 119.39(14), C25-P2-C37 102.76(18).

relatively short Ge–P distance (2.291(4) Å) is also observed in the two-coordinate phosphagermylene [2,6-(Tripp)$_2$C$_6$H$_3$]Ge[P(SiMe$_3$)$_2$] (**4**), although this compound contains a pyramidal phosphorus center and so does not possess significant Ge–P multiple bond character (Tripp = 2,4,6-iPr$_3$C$_6$H$_2$).[7d] The Ge–P1 distance in **2** is somewhat longer than the corresponding distances in previously reported phosphagermene compounds, although we note that these involve a Ge^{IV}=P double bond; for example, the Ge–P distances in (Mes)$_2$Ge=P(Mes*) (**5**)[15] and (tBu$_2$MeSi)$_2$Ge=P(Mes*) (**6**)[16] are 2.138(3) and 2.1748(14) Å, respectively (Mes = 2,4,6-Me$_3$C$_6$H$_2$, Mes* = 2,4,6-tBu$_3$C$_6$H$_2$). The P1-Ge-P2 angle of 107.40(4)° is similar to the P-Ge-C angle (106.89(5)°) in **4**.[7d]

In solution, **2** is highly fluxional; the ^{1}H NMR spectrum of **2** at room temperature exhibits a single set of broad signals, consistent with rapid exchange between the two (Dipp)$_2$P ligands and with rapid rotation about the P–C bonds. At low temperatures these signals broaden and decoalesce, such that, at −95 °C, the spectrum consists of numerous broad overlapping signals that are not possible to assign unambiguously. The ^{31}P{^{1}H} NMR spectra of **2** are more informative: at room temperature, a single, broad singlet is observed at 3.2 ppm (Figure 2), which is consistent with rapid exchange between
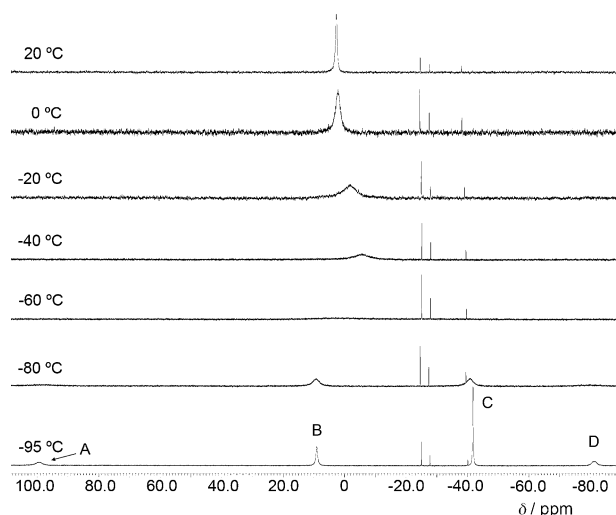
Figure 2. Variable temperature ^{31}P{^{1}H} NMR spectra of **2** in [D$_8$]toluene [the low intensity peaks between −20 and −40 ppm are due to minor impurities].

two phosphorus centers in **2** are distinctly different: while P2 adopts a typical trigonal pyramidal geometry (sum of angles at P2 = 311.53°), with its lone pair directed towards the rear of the molecule, P1 is essentially planar (sum of angles at P1 = 358.35°) and the C1-P1-C13 and P1-Ge-P2 planes are nearly coincident. Furthermore, while the Ge–P2 distance (2.3823(12) Å) is similar to previously reported Ge^{II}–P distances,[5–7] the Ge–P1 distance is approximately 6% shorter (2.2337(11) Å). This is consistent with a significant degree of multiple bond character in the Ge–P1 bond (**IV**, Scheme 1); for comparison, the Ge–P distance in [CH-{MeCN(Dipp)}$_2$]Ge[P(SiMe$_3$)$_2$] (**3**) is 2.3912(8) Å.[7a,14] A

the pyramidal and planar phosphorus centers. As the temperature is reduced this signal broadens and shifts to higher field, until, at −80 °C, the signal decoalesces into two broad, equal intensity singlets at 8.0 and −42.0 ppm, along with two very broad, low intensity signals at approximately 95 and −80 ppm. These signals sharpen as the temperature is reduced further, such that at −95 °C (the lowest temperature that we were able to attain) the spectrum consists of broad singlets at 98.5 (**A**), 7.8 (**B**), −43.1 (**C**), and −82.0 ppm (**D**) in the ratio 1:2:3:1; coupling between the ^{31}P nuclei is not resolved. A ^{31}P EXSY NMR spectrum at this temperature shows that there is rapid exchange between **A** and **D** and between **B** and **C**, but not

between the pairs **A/D** and **B/C** (see Supporting Information).

The $^{31}P\{^1H\}$ CP-MAS solid-state NMR spectrum of **2** exhibits peaks with isotropic chemical shifts of 81.9 and −61.6 ppm in a 1:1 ratio, the former exhibiting substantial chemical shift anisotropy consistent with a planar phosphorus environment; no other significant signals are observed (see the Supporting Information for further details). Compounds with a planar phosphorus center involved in a Ge^{IV}=P bond typically have downfield ^{31}P chemical shifts (for example, 175.4 (**5**), 416.3 (**6**) ppm),[15,16] while diphosphagermylenes with pyramidal phosphorus centers typically have ^{31}P chemical shifts close to those of the free phosphine.[5,6] We therefore assign the broad signals **A** and **D** in the low-temperature solution-state spectrum (and the corresponding signals at 81.9 and −61.6 ppm in the solid-state NMR spectrum) to the planar and pyramidal phosphorus centers in **2**, respectively. This assignment is supported by DFT calculations (see below), which predict chemical shifts for the planar and pyramidal phosphorus centers in **2** of 100 and −61 ppm, respectively (see the Supporting Information for details). The identity of the species that account for signals **B** and **C** is less clear. These signals appear to arise from two separate species owing to their unequal intensities. As all four peaks **A**–**D** coalesce to a single peak at room temperature and as both elemental analysis and solid-state ^{31}P NMR data indicate the presence of a single species in the solid state, we attribute peaks **B** and **C** to alternative conformers of **2**, each possibly containing two pyramidal phosphorus centers; however, on the current evidence it is not possible to confirm this.

DFT calculations provide further insight into the nature of the bonding in **2**. The calculated structure (**2$_{calc}$**) at the B97D/6-311G(2d,p) level of theory is very similar to that obtained by X-ray crystallography. In particular, the planar nature of one phosphorus center is reproduced extremely well; the sum of angles about P1 in **2$_{calc}$** is 359.71°.

Inspection of the MOs reveals that the HOMO and LUMO are centered on the aromatic rings of the Dipp substituents. However, the HOMO−1 consists of a π-orbital arising from overlap of a phosphorus lone pair of essentially pure p-character with the vacant p-orbital on the germanium atom (Figure 3). Natural bond orbital analysis indicates that
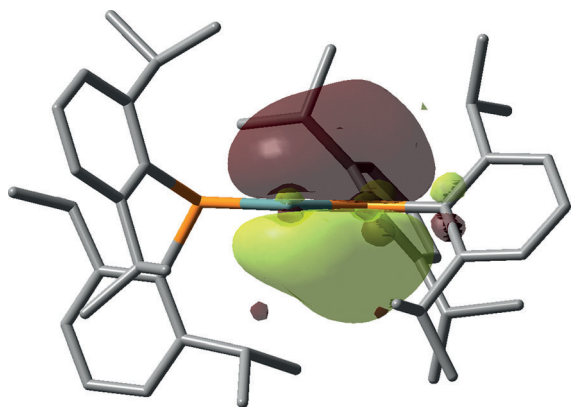
this orbital lies just 0.3 eV higher in energy than the P−Ge σ bond and that it is 77% P-based. The corresponding π* orbital is found as the LUMO + 1 and lies 0.3 eV above the π-orbital. In contrast, the lone pair at P2 has essentially sp-character and is oriented towards the rear of the molecule, while the germanium lone pair has predominantly s-character.

Consistent with the presence of Ge−P1 multiple bond character, the Wiberg bond indices for the Ge−P1 and Ge−P2 bonds are 1.33 and 0.89, respectively. Analysis of the bonding in **2$_{calc}$** using the atoms-in-molecules approach similarly indicates the presence of double bond character in the Ge−P1 bond.[17] A bond critical point (BCP) was located between Ge and P1 with $\rho = 0.091$ and ellipticity 0.297, compared with the BCP between Ge and P2 with $\rho = 0.083$ and ellipticity 0.064. The ellipticity is a quantitative measure of the anisotropy of the electron density (that is, its deviation from cylindrical symmetry) at the BCP and provides information on the π-character of the bond; for example, the ellipticities of the C−C, C=C, and C≡C bonds in butane, ethylene, and ethyne are 0.01, 0.30, and 0.00, respectively.[18] Thus, the Ge−P2 bond has essentially single bond character, while the Ge−P1 bond has substantial double bond character. An alternative estimate of bond order may be obtained from the delocalization index (DI), which is equivalent to a bond order when two atoms are connected by a bond path;[19] for the Ge−P1 and Ge−P2 bonds the DIs are calculated to be 1.275 and 0.843, respectively, which is consistent with the Wiberg bond orders obtained for these bonds.[20]

Attempts to locate a minimum energy geometry in which both phosphorus centers were pyramidal, and which might shed light on the species observed in the low-temperature $^{31}P\{^1H\}$ NMR spectrum of **2**, were unsuccessful. These led only to the identification of a second conformer, **2′$_{calc}$**, in which the two aromatic rings adjacent to the planar P center are twisted in the opposite direction; this second conformer lies just 1.9 kJ mol^{-1} higher in energy than **2$_{calc}$**.

In summary, we report the synthesis of a uniquely sterically hindered phosphanide ligand and its use in the synthesis of the first diphosphatetrylene with a trigonal planar P atom. DFT calculations indicate that the electron-poor germanium(II) center in this compound is stabilized by delocalization of the lone pair of the planar phosphorus atom into the vacant p-orbital at germanium, effectively generating a Ge=P π-interaction.

Figure 3. HOMO−1 of **2$_{calc}$** showing the P-Ge π-orbital.

Experimental Section

Synthesis of (Dipp)$_2$PH (**1**): PCl$_3$ (0.85 mL, 1.34 g, 9.7 mmol) was added dropwise by syringe to a solution of (Dipp)Li(OEt$_2$)[12] (4.74 g, 19.6 mmol) in cold (0°C) diethyl ether (40 mL). This mixture was allowed to attain room temperature and was stirred for 16 h. The solids were removed by filtration and volatiles were removed in vacuo from the filtrate to give a sticky yellow solid. This was dissolved in diethyl ether (30 mL) and this solution was added dropwise to a suspension of LiAlH$_4$ (0.37 g, 9.7 mmol) in diethyl ether (10 mL), and this mixture was stirred for 3 h. Degassed water (30 mL) was carefully added and the organic phase was extracted into diethyl ether (3 × 20 mL) and dried over activated 4 Å molecular sieves. The dried solution was filtered and solvent was removed in vacuo from the

filtrate to give **1** as a colorless solid. Yield 2.63 g, 76%. ^{1}H NMR (CDCl$_3$): $\delta = 1.01$ (d, $J_{HH} = 6.4$ Hz, 12 H, CH*Me*Me), 1.04 (d, $J_{HH} = 6.9$ Hz, 12 H, CHMe*Me*), 3.51 (m, 2 H, C*H*MeMe), 5.47 (d, $J_{PH} = 232.6$ Hz, 1 H, PH), 7.08 (m, 2 H, ArH), 7.24 ppm (m, 1 H, ArH). ^{13}C{^{1}H} NMR (CDCl$_3$): $\delta = 23.85$ (CH*Me*Me), 24.26 (CHMe*Me*), 32.84 (d, $J_{PH} = 12.5$ Hz, *C*HMeMe), 123.54, 128.83, 132.75 (Ar), 152.61 ppm (d, $J_{PC} = 11.0$ Hz, Ar). ^{31}P NMR (CDCl$_3$): $\delta = -101.1$ ppm (d, $J_{PH} = 232.6$ Hz).

Synthesis of (Dipp$_2$P)$_2$Ge (**2**): A solution of PhCH$_2$K[21] (0.42 g, 3.3 mmol) in THF (10 mL) was added to a solution of **1** (1.13 g, 3.2 mmol) in THF (30 mL) and this mixture was stirred for 2 h. The resulting red solution was added dropwise to a solution of GeCl$_2$(1,4-dioxane) (0.37 g, 1.6 mmol) in THF (10 mL). This mixture was stirred for 16 h in the absence of light. Solvent was removed in vacuo and the sticky red solid was extracted into toluene (40 mL) and filtered. The filtrate was concentrated to about 5 mL and cooled to $-20\,^\circ$C; dark red blocks of **2** suitable for X-ray crystallography were isolated after 2 weeks. Yield 0.47 g, 38%. Anal. calcd. for C$_{48}$H$_{68}$GeP$_2$ (779.58): C 73.95, H 8.79%; found C 73.81, H 8.72%. ^{1}H NMR ([D$_8$]toluene, 295 K): $\delta = 1.08$ (br. s, 48 H, CH*Me*$_2$), 3.94 (br. s, 8 H, C*H*Me$_2$), 6.99 (m, 8 H, ArH), 7.11 ppm (m, 4 H, ArH). ^{13}C{^{1}H} NMR ([D$_8$]toluene, 295 K): $\delta = 24.73$ (CH*Me*$_2$), 34.14 (*C*HMe$_2$), 124.45, 129.13, 137.61, 153.38 ppm (Ar). ^{31}P{^{1}H} NMR ([D$_8$]toluene, 295 K): $\delta = 3.2$ ppm (br. s).

DFT calculations: Geometry optimizations were performed with the Gaussian 09 suite of programs (revision D.01) using the B97D functional, which includes a correction for dispersion effects, and with automatic density fitting; the 6-311G(2d,p) all-electron basis set was used on all atoms (default parameters were used throughout). The location of minima was confirmed by the absence of imaginary vibrational frequencies. NMR shielding tensors were calculated for the optimized structure using the GIAO method at the B97D/6-311 + + G(2d,p) level of theory and chemical shifts are quoted relative to 85% H$_3$PO$_4$. Natural bond orbital analyses were performed using the NBO 3.1 module of Gaussian 09. Further details of these calculations can be found in the Supporting Information.

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[21] Details of the synthesis of this compound are given in the Supporting Information.