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Crystal structure of the phosphanylidene-σ^4-phosphorane DmpP=PMe$_3$ (Dmp = 2,6-Mes$_2$C$_6$H$_3$) and reactions with electrophiles

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Abstract

The stable phosphanylidene-σ^4-phosphorane DmpP=PMe$_3$ (**1**, Dmp = 2,6-Mes$_2$C$_6$H$_3$) has been examined by single-crystal X-ray diffraction methods. The structure of **1** features a relatively short P–P bond length of 2.084(2) Å. Reactions of **1** with various electrophiles demonstrate the nucleophilic behavior of the phosphanylidene atom of **1** and also provide access to new organophosphorus compounds. For example, addition of excess BH$_3$ (in the form of either BH$_3$·THF or BH$_3$·SMe$_2$) to **1** leads to formation of a mono-borane adduct DmpP(BH$_3$)PMe$_3$. Reactions of carbon and silicon based electrophiles EX (E = R$_3$C or R$_3$Si; X = halide or OTf$^-$) produce either diphosphanium salts [DmpP(E)PMe$_3$]X or phosphines DmpP(E)X. In some cases equilibrium mixtures of both product types are observed, and the equilibria can be shifted by addition of either X$^-$ or PMe$_3$. Compound **1** is also readily protonated by HOTf, HCl and PhOH. As found for the carbon and silicon based electrophiles, the nature of the resulting product depends on the counterion. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Phosphorus; Phosphanylidene-σ^4-phosphorane; Diphosphanium; Phosphinidene; Electrophile addition

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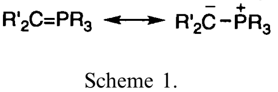
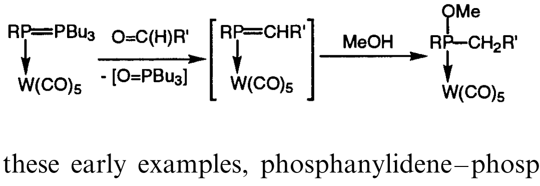
1. Introduction

Neutral phosphanylidene-σ^4-phosphoranes (R′P=PR$_3$) can be envisioned as adducts of phosphinidenes and phosphines. These fascinating main group phosphinidene complexes, despite their initial identification in 1961[1], still remain limited in number [2]. Although not bearing true p–p π double bonds, the resonance structures drawn to represent the bonding in phosphanylidene-σ^4-phosphoranes bear a great resemblance to the resonance structures used to represent the bonding in the better-known and synthetically important Wittig reagents (Scheme 1) [3].



Scheme 1.

Materials that do possess true p–p π double bonds involving phosphorus atoms show significant parallels to the chemistry of analogous materials having carbon–carbon double bonds [4]. These facts suggest that phosphanylidene-σ^4-phosphoranes might have other features in common to Wittig reagents in terms of structure and reactivity. In particular, such species might have utility for the construction of P=C bonds, just as Wittig reagents serve to build C=C bonds [5]. In fact, Mathey has pioneered the ‘phospha-Wittig’ reaction, as portrayed in Eq. (1) [5–7].


(1)

In these early examples, phosphanylidene–phosphoranes containing relatively unhindered ligands were stabilized by coordination to a metal center. The metal serves as a means to prevent oligomerization of the

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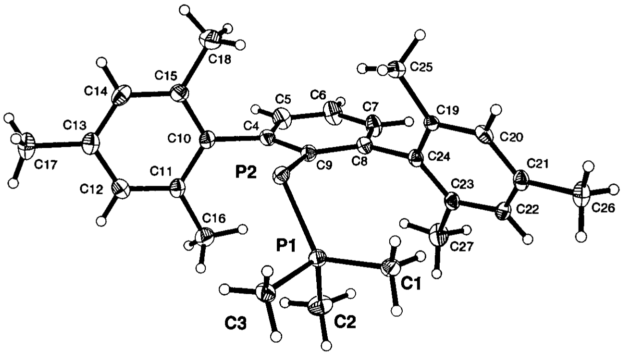
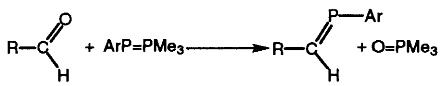


Fig. 1. Thermal ellipsoid plot for DmpP=PMe$_3$ (**1**). Selected bond distances (Å) and angles (°): P(1)–P(2), 2.084(2); P(2)–C(9), 1.843(4); P(1)–C(1), 1.797(4); P(1)–C(2), 1.804(4); P(1)–C(3), 1.805(4); C(9)–P(2)–P(1), 106.79(13); C(1)–P(1)–P(2), 121.5(2); C(2)–P(1)–P(2), 117.4(2); C(3)–P(1)–P(2), 102.3(2).

phosphinidene to oligomeric species (RP)$_n$. The metal also serves to render stability to the resulting phosphaalkenes. We have recently demonstrated that easily prepared and kinetically stabilized phosphanylidene-σ^4-phosphoranes of the form ArP=PR$_3$ (Ar = 2,4,6-^{t}Bu$_3$C$_6$H$_2$ (Mes*) or 2,6-Mes$_2$C$_6$H$_3$ (Dmp), R = Me or ^{n}Bu) can be isolated as free species, and furthermore, shown that indeed they act as efficient ‘phospha-Wittig’ reagents for transforming aldehydes to phosphaalkenes (Eq. (2)) [8,9].



$$\mathrm{R{-}C({=}O)H} + \mathrm{ArP{=}PMe_3} \longrightarrow \mathrm{R{-}C({=}P{-}Ar)H} + \mathrm{O{=}PMe_3} \qquad (2)$$

Although phosphanylidene-σ^4-phosphoranes are not new, some aspects of their reactivity are not well understood. For example, the best known representatives of this class of materials are the originally discovered CF$_3$P=PMe$_3$ [1,10–12] and the novel phosphino-functionalized derivatives ^{t}Bu$_2$PP=PR′R$_2$ [13–27]. Reactions of either CF$_3$P=PMe$_3$ or ^{t}Bu$_2$PP=PR$_3$ with aldehydes or ketones to form phosphaalkenes, however, do not appear to have been reported [25,28].

Other differences in reactivity for neutral phosphanylidene-σ^4-phosphoranes can be noted. For example, ^{t}Bu$_2$PP=PMe^{t}Bu$_2$ and ^{t}Bu$_2$PP=P(Br)^{t}Bu$_2$ decompose in the presence of olefins to form cycloadducts. Interestingly, the former species decomposes above −30°C, while the latter decomposes only at room temperature and above. These reactions provide evidence for generation of the free phosphinophosphinidene ‘^{t}BuPP’. By contrast, DmpP=PMe$_3$, although decomposing slowly at room temperatures and above, does not react with either neat cyclohexene or isoprene. Reactions of electrophiles illustrate some other differences. For example, reactions of alkylating reagents (RX) with CF$_3$P=PMe$_3$ yield products derived from diphosphanium salts [CF$_3$(R)PPMe$_3$]X [10], while reactions of ^{t}Bu$_2$PP=P(Br)^{t}Bu$_2$ with P-electrophiles such as ^{t}BuPhPCl result in the products of phosphine exchange ^{t}Bu$_2$PP=P(Cl)^{t}BuPh [23]. Despite these differences, it should be noted that all three classes of neutral phosphanylidene-σ^4-phosphoranes undergo facile trialkylphosphine exchange reactions (Eq. (3)) [8,12,23].

$$\mathrm{RP{=}PR'_3} + \mathrm{PR''_3} \rightleftharpoons \mathrm{RP{=}PR''_3} + \mathrm{PR'_3} \qquad (3)$$

The chemistry of neutral phosphanylidene-σ^4-phosphoranes thus is dependent upon the nature of the groups within the molecule. DmpP=PMe$_3$ (**1**) was first identified in the reaction of [Cp$_2$Zr=PDmp(PMe$_3$)] (Dmp = 2,6-Mes$_2$C$_6$H$_3$) with DmpPCl$_2$ [29,30]. During efforts to delineate the mechanism by which DmpP=PMe$_3$ is formed from the zirconium phosphinidene complex, it also became critical to clarify the fundamental chemistry of **1** with electrophiles. Herein we report the crystal structure of **1**, as well as reactions of **1** with electrophiles that provide access to a range of new materials.

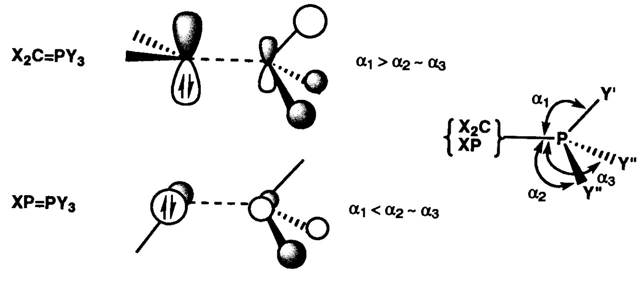
2. Results and discussion

2.1. Structure of DmpP=PMe$_3$ (1)

DmpP=PMe$_3$ is readily synthesized by reduction of the corresponding aryldichlorophosphine DmpPCl$_2$ [31] with zinc in the presence of PMe$_3$ [8]. Having demonstrated the reactivity of **1** with aldehydes, a detailed structure was desired. Single crystals of **1** were grown from hexanes and the results of an X-ray structural analysis is displayed in Fig. 1. The most prominent feature of **1** is the short P–P bond length of 2.084(2) Å. This value is clearly shorter than typical data obtained for P–P single bonds (ca. 2.22 Å) and approaches the shorter end of such values [32]. Structural investigations of diphosphenes (RP=PR) having authentic P–P double bonds yield P=P bond lengths ranging from 1.985(2) to 2.034(1) Å [33,34]. Three other neutral acyclic phosphanylidene-σ^4-phosphoranes have been structurally characterized. The structures of ^{t}Bu$_2$PP=PMe^{t}Bu$_2$, ^{t}Bu(Me$_3$Si)PP=PMe^{t}Bu$_2$ and ^{t}Bu$_2$PP=PBr^{t}Bu$_2$ display P=P bond lengths of 2.1263(2), 2.1358(5) and 2.077(2) Å, respectively [17,20]. Each species accordingly has somewhat longer P–P single bonds that range from 2.1791(4) to 2.202(2) Å. The angles about each two-coordinate phosphorus atom of 100.951(13), 100.29(2) and 105.77(7)°, respectively, are slightly smaller than the corresponding value of 106.79(13)° for **1**. Cationic analogues, such as the triphosphenium species [Ph$_3$PP=PPh$_3$]AlCl$_4$ [35] show lengthened P=P bond lengths by comparison (ca. 2.12–2.14 Å), possibly due to delocalization effects [2]. The structure of a novel tungsten-stabilized phosphanylidenephosphorane [(CO)$_5$W{EtO(O)CP=PEt$_3$}] has also been determined and shown to have a somewhat elongated P=P bond length of 2.156(2) Å [36]. The structural features of the sterically encumbering *meta*-terphenyl group are in accord with the unique ability of such ligands to stabilize low-coordinate and multiply bonded main group elements [37].

As mentioned above, the P–P bond length in **1** nearly falls into the range expected for true phosphorus–phosphorus π-bonds and suggests partial multiple bonding between the phosphorus atoms and significant contributions from the resonance structure shown on the left in Scheme 1. Alternatively, the shortened P–P bond may be a result of electrostatic attractions between the oppositely charged phosphorus atoms (the resonance structure shown on the right in Scheme 1). Likewise, the P–C distances in Wittig reagents (R'_2CPR_3), compounds that share similar resonance structures to phosphanylidene-σ^4-phosphoranes, are often notably shorter than P–C single bonds. The nature of the bonding Wittig reagents has received a quite deal of attention and has been tackled by numerous theoretical calculations [38–40]. Expectedly, some of the results can be paralleled to the bonding in **1**. Studies at the MP2/6-31G* and MP4/6-31G** levels of theory have predicted P–P bond lengths of 2.087 and 2.099 Å, respectively, for $HPPH_3$ [41,42]. The electronic structures of $R_2PP{=}P(X)R_2$ have also been probed by ab intio methods [17]. All of these calculations suggest substantial partial charges on the phosphorus atoms for the $XP{=}PY_3$ fragments. The HOMO in these materials is dominated by the presence of the phosphanylidene p orbital that is heavily polarized toward the phosphorane center.

In the related Wittig species, the analogous carbene p orbital appears to engage in a π- bonding interaction by back donation into empty P–Y σ* molecular orbitals (Scheme 2, upper diagram) [3,39,43]. This negative hyperconjugation results in distortions of the phosphorane geometry that have been previously detailed [43]. In summary, if the filled p-orbital interacts with the phosphorane P–Y σ* orbitals of appropriate symmetry in the orientation as shown in Scheme 2, upper diagram (the most common solid-state geometry for Wittig reagents), then a distortion of the phosphorane is predicted to result in one large and two smaller C–P–Y angles ($\alpha_1 > \alpha_2 \sim \alpha_3$, a 'negative tilt') [43]. This distortion has been observed in some structurally characterized Wittig species.



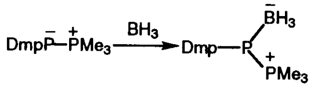
Scheme 2.

If, on the other hand, the filled p-orbital interacts with the phosphorane P–Y σ* orbitals of appropriate symmetry in the orientation as shown in Scheme 2, lower diagram, then a distortion of the phosphorane is predicted to result in one small and two larger C–P–Y angles ($\alpha_1 < \alpha_2 \sim \alpha_3$, a 'positive tilt'). A complete explanation of this prediction is somewhat more complicated and requires consideration of filled–filled interactions [43].

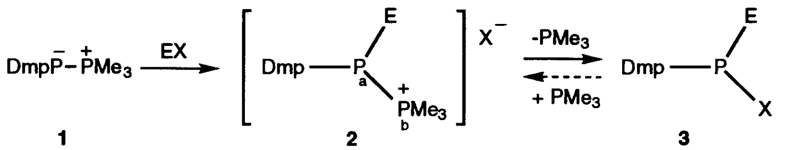
As predicted by theory for $HPPH_3$ [41,42], **1** adopts a geometry that is closer to that represented by the bottom structure in Scheme 2. The structure deviates slightly from the idealized structure portrayed in that one methyl group is offset by 21.8° from a perfect anti orientation to the Dmp group. Interestingly, theory predicts a small rotational barrier of 8.6 kcal mol^{-1} about the P–P bond in $HPPH_3$ [42], and thus, the observed structure may reflect subtle steric or crystal packing effects. As also predicted by the above bonding model, two of the angles about the phosphorane are substantially greater than the idealized tetrahedral angle of 109.5° (121.5(2) and 117.4(2)°). The angle involving the methyl group nearly anti to the Dmp group is substantially smaller (102.3(2)°). More structurally characterized examples of simple phosphanylidene-σ^4-phosphoranes are required in order to confirm the electronic issues described above. Arguments, and comparisons to **1**, regarding the 'tilting' of the phosphorane group in phosphino-substituted phosphanylidene-σ^4-phosphoranes are a bit more difficult to make owing to the asymmetric nature of the phosphoranes and more complicated structures.

2.2. Reactivity of 1 with electrophiles

The lone pairs of electrons (and possibly some negative charge) upon the phosphanylidene center of **1** forecasts facile reactions with electrophiles. Indeed, mixtures of **1** and $BH_3{\cdot}THF$ in THF readily produce $DmpP(BH_3)PMe_3$ (Eq. (4)), identified by its diagnostic ^{31}P-NMR spectroscopic properties (δ 5.2, −59.3 $J_{P\text{–}P} = 435$ Hz). Addition of 0.5 equivalents of $BH_3{\cdot}THF$ to **1** in THF produces an equimolar mixture of **1** and $DmpP(BH_3)PMe_3$ and corroborates the 1:1 stoichiometry of the reaction.



$$\mathrm{Dmp}\overset{-}{\mathrm{P}}{-}\overset{+}{\mathrm{P}}\mathrm{Me_3} \xrightarrow{\mathrm{BH_3}} \mathrm{Dmp}{-}\mathrm{P}(\overset{-}{\mathrm{B}}\mathrm{H_3})(\overset{+}{\mathrm{P}}\mathrm{Me_3}) \quad (4)$$



1 **2** **3**

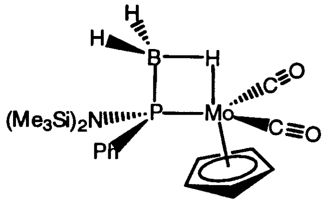
EX		^{31}P NMR (δ(a), δ(b))		^{31}P NMR (δ(a))
Me_3SiOTf	(**2a**)	-30.3, 15.7 (J_{PP} = 343 Hz)		
HOTf	(**2b**)	-93.0 (J_{PH} = 233 Hz), 17.3 (J_{PP} = 282 Hz)		
CH_3OTf	(**2c**)	-37.9, 16.7 (J_{PP} = 336 Hz)		
Me_3SiI	(**2d**)	-28.4, 17.0 (J_{PP} = 343 Hz)	(**3d**)	65.6
CH_3I	(**2e**)	-36.6, 18.2 (J_{PP} = 336 Hz)	(**3e**)	49.2
HCl			(**3f**)	24.5 (J_{PH} = 206 Hz)
PhOH			(**3g**)	80.4 (J_{PH} = 220 Hz)

Scheme 3.

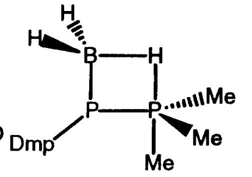
Borane-adducts of $CF_3P{=}PMe_3$ have been reported [11]. Interestingly, unlike $CF_3P{=}PMe_3$, **1** shows no proclivity for addition of a second BH_3 unit even upon addition of excess BH_3·THF. The inability to generate a bis-borane adduct might be attributable to the greater steric hindrance about **1** as compared to $CF_3P{=}PMe_3$. Interestingly, $DmpP(BH_3)PMe_3$ is also produced by the reaction of BH_3·SMe_2 and **1** in THF. No products of phosphinidene transfer to sulfur, such as $DmpP{=}SMe_2$, were detected. Although the reaction of **1** with these sources of BH_3 in THF are initially clean by ^{31}P-NMR, attempts to isolate $DmpP(BH_3)PMe_3$ have been thwarted by its instability in solution. This result contrasts to the apparent increased stability of $CF_3P(BH_3)PMe_3$ relative to $CF_3P{=}PMe_3$. Reactions of **1** with either BH_3·THF or BH_3·SMe_2 in relatively non-polar solvents such as hexanes, Et_2O, or C_6D_6 show different reactivity patterns and are dependent on the number of equivalents of borane added.

Other reactions with boranes were either unproductive or too complicated for clear analysis. For example, mixtures of **1** and ten equivalents BEt_3 in either THF or C_6D_6 show no evidence of reaction. By contrast, **1** undergoes slow reaction with excess BF_3·Et_2O in THF to afford a material tentatively identified as $DmpP(BF_3)PMe_3$ (^{31}P-NMR: δ 16.1, −28.9 (J_{PP} = 352 Hz)), however, this mixture is even more complicated than the reactions of **1** with BH_3. Likewise, **1** shows evidence for slow reaction with excess BPh_3 in THF; however, spectral signatures attributable to a species such as $DmpP(BPh_3)PMe_3$ could not be seen amongst the signals observed in the complicated mixtures thus formed.

Another intriguing possibility for the structure of $DmpP(BH_3)PMe_3$ can be proposed based on the results of the study of the reaction product of [Cp-$Mo(CO)_2\{P(Ph)N(SiMe_3)_2\}$] with BH_3·THF (**I**, below) [44].



I



II

In **I** the multiple bonding between the metal center and the phosphorus atom has been interrupted by addition of the borane and the 16 electron molybdenum center thus engages one of the hydrides to achieve an 18 electron configuration. Likewise, one could draw a similar structure for $DmpP(BH_3)PMe_3$ where the electropositive phosphorane interacts with a hydride ligand (**II**) to become pentacoordinate. Although there is no NMR evidence to confirm this mode of stabilization for $DmpP(BH_3)PMe_3$, there is a notably higher PP coupling constant for $DmpP(BH_3)PMe_3$, relative to the diphosphanium species $[DmpP(E)PMe_3]X$ presented below (J_{PP} = 435 Hz versus J_{PP} = 282–343 Hz). The exact role of such a structure in stabilization or adding complexity to these reaction mixtures remains unclear at this time.

Reactions of **1** with electrophiles produce new diphosphanium (alternatively described as phosphinephosphenium or phosphinophosphonium) salts **2** and phosphines **3** (Scheme 3). The nature (and distribution) of the products formed in these reactions depends on the electrophile and reaction conditions. Diphosphanium salt formation appears to be promoted by the presence of relatively non-coordinating anions such as triflate. Thus, reactions of **1** with Me_3SiOTf, triflic acid, and methyl triflate produce as the major products **2a**–**2c**, respectively. These materials are readily identified by ^{31}P-NMR spectroscopy and phosphorus–phosphorus coupling constants that verify that the phosphorus–phosphorus linkage is still intact. For example, upon methylation of **1** (^{31}P δ −2.8 and −114.7, $J_{PP} = 582$ Hz) by MeOTf, a new set of ^{31}P-NMR doublets at δ 16.7 and −37.9 ($J_{PP} = 336$ Hz) in benzene-d_6 appears for **2c**. A recent report has described the methylation of Mes*P=PMes* (Mes* = 2,4,6-$^{t}Bu_3C_6H_2$) by excess MeOTf to produce a stable phosphanyl phosphenium ion [45]. As is consistent with the phosphanylidene signal appearing upfield in **1**, the tricoordinate phosphorus atom in compounds **2** also show upfield resonances in the ^{31}P-NMR spectra. This is well adduced by compound **2b**, whereby proton coupling is observed for the upfield resonance. The connectivity of compound **2c** was also confirmed by a preliminary single crystal structural determination [46]. Unfortunately, crystal decay problems thwarted a proper structural characterization. Regardless, an ion separated species and a trigonal geometry ($\Sigma_{BA}(P) = 315°$) for the methylated phosphorus center is confirmed, and tentatively, a P–P bond distance of 2.180 Å can also be assigned.

Reactions of **1** with electrophiles can be more complex when the anion of the electrophile exhibits an affinity for the diphosphanium species comparable to trimethylphosphine. For example, addition of either Me_3SiI or MeI to **1** produces mixtures of diphosphanium salts $[DmpP(E)PMe_3]I$ and the iodophosphines DmpP(E)I. NMR analysis of such mixtures shows two distinct sets of resonances. Although these two species are not equilibrating rapidly on the NMR timescale, equilibration does occur. For example, addition of PMe_3 to a mixture of **2e** and **3e** (THF) increases the concentration of **2e** at the expense of **3e**. Similarly, equilibrium ratios of these two types of products can be generated by the addition of KI to solutions of $[DmpP(SiMe_3)PMe_3]OTf$ or $[DmpP(Me)PMe_3]OTf$. Qualitatively, non-polar solvents appear to shift the equilibria to favor **3**, while polar solvents favor **2**. A more quantitative study of this equilibrium process was impeded by secondary reactions of PMe_3 with MeI and Me_3SiI.

By comparison, alkylation of $CF_3P{=}PMe_3$ by MeI also leads to a product tentatively assigned as the diphosphanium salt $[CF_3(Me)PPMe_3]I$ (Eq. (5)) [10]. This material was not characterized, but addition of HCl to this material induces loss of $[HPMe_3]I$ and yields the mixed chlorophosphine $CF_3(Me)PI$.

$$\begin{aligned}&CF_3P{=}PMe_3 + MeI\\&\rightarrow \{[CF_3(Me)PPMe_3]I\} \xrightarrow[-\,[HPMe_3]I]{HCl} CF_3(Me)PCI \qquad (5)\end{aligned}$$

Unlike the above reactions, reactions of **1** with the proton sources HCl, phenol and water were simpler. The first two reagents produced the novel secondary phosphines DmpP(H)Cl (**3f**) and DmpP(H)OPh (**3g**). In particular, secondary phosphines of the form RP(H)Cl, such as DmpP(H)Cl, are few in number and access to such species is rather limited [47]. Using our procedure, pure crystalline **3d** can be isolated in 57% yield. Likewise, addition of phenol across the phosphanylidene center occurs to afford pale yellow DmpP(H)OPh in 89% isolated yield. The anticipated initial product of water addition to **1**, DmpP(H)OH, apparently rapidly tautomerizes to the more thermodynamically favored phosphine oxide $DmpP(O)H_2$. This new material can also be prepared independently by the oxidation of $DmpPH_2$ by aqueous hydrogen peroxide. The ^{31}P-NMR properties of $DmpP(O)H_2$ (^{31}P-NMR ($CDCl_3$) δ −11.5 (t, $J_{PH} = 483$ Hz)) are essentially equivalent to the related sterically encumbered phosphine oxide Mes*$P(O)H_2$ (^{31}P-NMR ($CDCl_3$) −10.0 (t, $J_{PH} = 491$ Hz)) that has been prepared by this method [48].

2.3. Attempted synthesis of $[DmpP(Cl)PMe_3]Cl$ and generation of $[DmpP(H)PMe_3]^+$

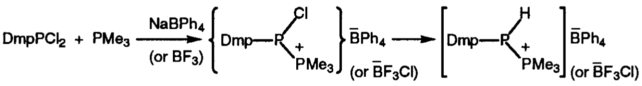
A major diving force for the present study was the need to address the influence of PMe_3 upon the reaction of $[Cp_2Zr{=}PDmp(PMe_3)]$ with $DmpPCl_2$. In particular, reaction rates are increased and the main product becomes **1** upon increasing concentrations of PMe_3 [29]. As added PMe_3 did not show any evidence for reaction with the zirconium species, we suspected that reaction of $DmpPCl_2$ with PMe_3 may lead to a diphosphanium species of the form $[DmpP(Cl)PMe_3]Cl$ that may be more reactive with $[Cp_2Zr{=}PDmp(PMe_3)]$ than $DmpPCl_2$. This proposal seemed reasonable in light of the fact that excess PMe_3 reacts (albeit slowly) with $DmpPCl_2$ to produce **1** (Eq. (6)) [8].

$$DmpPCl_2 + \text{xs } PMe_3 \rightarrow Dmp{=}PMe_3 + Me_3PCl_2 \qquad (6)$$

One likely initial product of PMe_3 and $DmpPCl_2$ can be postulated as $[DmpP(Cl)PMe_3]Cl$. Diphosphanium salts have been implicated as the initial intermediates in trialkylphosphine promoted chlorine atom abstraction processes that produce new P–P single bonds [49–52]. For example, reaction of triethylphosphine with dichloromethylphosphine proceeds, as shown in Eq. (7), to yield the diphosphanium salt $[MeP(Cl)PEt_3]Cl$, which can be isolated and heated in refluxing hexane to yield Et_3PCl_2 and the cyclopentamer of methylphosphinidene [50].

$$MePCl_2 + PEt_3 \rightarrow [MeP(Cl)PEt_3]Cl \xrightarrow{\Delta} (MeP)_5 + Et_3PCl_2 \qquad (7)$$

Attempts to either isolate, or even observe $[DmpP(Cl)PMe_3]Cl$, however, have proven difficult. For example, ^{31}P-NMR analysis of equimolar solutions of PMe_3 and $DmpPCl_2$ show that complex mixtures are formed, sometimes containing **1** and Me_3PCl_2, the nature and distribution of which depends greatly on the solvent. In select solvents (such as dichloromethane and acetonitrile) the major product is $[DmpP(H)PMe_3]^+$, the same material which we have independently characterized above. The reaction of PMe_3 and $DmpPCl_2$ in the presence of chloride acceptors such as $NaBPh_4$ or $BF_3 \cdot THF$ were also investigated with hopes of stabilizing the $[DmpP(Cl)PMe_3]^+$ cation. Such mixtures even more rapidly produce $[DmpP(H)PMe_3]^+$ as the major product, and not the anticipated $[DmpP(Cl)PMe_3]^+$ cation (Eq. (8)).



(8)

Conducting the reaction of one equivalent of PMe_3 and $DmpPCl_2$ in $CDCl_3$ produces $[DmpP(D)PMe_3]^+$ ($J_{DP} = 84$ Hz), indicating that the hydrogen atom arises from solvent abstraction. The reasons for the instability of $[DmpP(Cl)PMe_3]^+$ are unclear, but well characterized examples of the form $[RP(Cl)PR_3]^+$ remain very few in number [53,54].

These results, however, suggest the possibility that $[DmpP(H)PMe_3]^+$ might be a viable alternative to $[DmpP(Cl)PMe_3]^+$ as an intermediate in the reaction of $DmpPCl_2$ and excess PMe_3 to form **1** (Eq. (6)). Deprotonation of $[DmpP(H)PMe_3]^+$ by excess PMe_3 could thus result in **1** and $[HPMe_3]^+$. Addition of PMe_3 to independently prepared and purified $[DmpP(H)PMe_3]$-OTf (**2b**) showed little signs of reaction at room temperature, and suggests that $[DmpP(H)PMe_3]^+$ is not an intermediate in Eq. (6).

3. Conclusions

An unusually stable neutral phosphanylidene-σ^4-phosphorane $DmpP{=}PMe_3$ has been structurally characterized. The structure reveals a short P–P bond length of 2.084(2) Å, and careful examination of the phosphorane geometry of **1** suggests a possible role of negative hyperconjugation for imparting some degree of π-bonding character between the phosphorus atoms. Alkylation or protonation of the phosphanylidene atom in **1** by electrophiles provides a variety of new organophosphorus species. In many ways, the reactions of **1** can be compared to studies of metal phosphenium complexes with electrophiles [55,56]. Additionally, the diphospanium cations in salts **2** can be contrasted to various examples of other low-coordinate cationic phosphorus compounds [54]. Further studies of the phosphinidene transfer reactions of these conveniently prepared phosphinidene-carriers such as **1** are underway.

4. Experimental

Inert condition manipulations were conducted in a drybox or Schlenk line under a nitrogen atmosphere. THF, hexanes and diethyl ether were purified by distillation from purple or deep blue Na-benzophenone solutions under N_2. Acetonitrile and CH_2Cl_2 were dried over calcium hydride and distilled. Phenol was freshly distilled prior to use. All other reagents were obtained from commercial sources in anhydrous form under nitrogen and used as received. ^1H- and ^{31}P-NMR spectra were recorded using a 300 MHz Varian Gemini spectrometer. ^{31}P-NMR spectra are referenced to external 85% H_3PO_4, while ^1H-NMR are referenced to residual proton solvent signals of $CDCl_3$ or C_6D_6. Mass spectroscopic analyses were performed at the CWRU departmental facility. $DmpP{=}PMe_3$ (**1**) was prepared as previously described [8].

4.1. Synthesis of $DmpP(BH_3)PMe_3$

To 200 mg (0.476 mmol) of **1** in 20 ml THF at −35°C was added 0.24 ml (0.48 mmol) of $BH_3 \cdot SMe_2$ (2.0 M in THF). The initial yellow solution color characteristic of **1** rapidly faded to give a clear solution. After stirring for 15 min all volatiles were removed under reduced pressure to give a white solid. ^{31}P-NMR (C_6D_6) δ 5.2 (d, $J_{PP} = 435$ Hz), −59.3 (d, $J_{PP} = 435$ Hz).

4.2. Synthesis of $[DmpP(SiMe_3)PMe_3]OTf$ (**2a**)

To 150 mg (0.357 mmol) of **1** in 15 ml THF was added 67 μl (0.370 mmol) of Me_3SiOTf. The initial yellow solution color of **1** progressively faded to give a pale yellow solution. After 4 h of stirring all volatiles were removed under reduced pressure to give a pale yellow–white waxy solid. ^{31}P-NMR spectroscopy indicates the solid to be ~90% pure in **2a**. Efforts to further purify the waxy solid were unsuccessful. ^{31}P-NMR (C_6D_6) δ 15.7 (d, $J_{PP} = 343$ Hz), −30.3, (d, $J_{PP} = 343$ Hz).

4.3. Synthesis of $[DmpP(H)PMe_3]OTf$ (**2b**)

To a solution of **1** (200 mg, 0.476 mmol) in 15 ml Et_2O was syringed 42 μl (0.476 mmol) of HOTf. As the initial yellow color characteristic of **1** faded, a white precipitate was produced. After 2 h, the reaction mixture was concentrated and the white precipitate was filtered, washed with hexanes, and vacuum dried to afford essentially pure **2b** (256 mg, yield 94%). ^{31}P-NMR (C_6D_6) δ 17.3 (d, $J_{PP} = 282$ Hz), −93.0 (dd, $J_{PP} = 282$, $J_{PH} = 233$ Hz). ^1H-NMR (C_6D_6) δ 6.96 (m, 1H), 6.87 (s, 2H), 6.76 (s, 2H), 6.70 (dd, 2H, $J_{HH} = 7.5$, $^4J_{HP} = 2.6$ Hz), 4.12 (dd, 1H, $J_{HP} = 232$, $^2J_{HP} = 9.1$ Hz), 2.17 (s, 6H), 1.99 (s, 6H), 1.82 (s, 6H), 1.40 (dd, 9H, $^2J_{HP} = 14.2$, $^3J_{HP} = 3.6$ Hz). HRMS(FAB) Calc.: 571.1965; Found: 571.2018.

4.4. Synthesis of [DmpP(CH_3)PMe_3]OTf (**2c**)

To a solution of 200 mg (0.476 mmol) of **1** in 20 ml Et_2O was added 54 μl (0.476 mmol) of MeOTf in 5 ml Et_2O. The initial yellow solution color characteristic of **1** turns clear and white precipitate progressively forms thereafter. The reaction mixture was allowed to stir for 1 h and then was concentrated by removing volatiles under reduced pressure. Upon reduction of reaction volume by half, the white precipitate was filtered and washed with hexanes and then vacuum dried to afford **2c** (256 mg, 92% yield). ^{31}P-NMR (C_6D_6) δ 16.7 (d), − 37.9 (d) ($J_{PP} = 336$ Hz). ^{1}H-NMR (C_6D_6) δ 6.93 (t, 1H, $J_{HH} = 7.6$ Hz), 6.77 (s, 2H), 6.75 (s, 2H), 6.60 (dd, 2H, $J_{HH} = 6.2$, $^4J_{HP} = 2.8$ Hz), 2.17 (s, 6H), 1.84 (s, 6H), 1.78 (s, 6H), 1.54 (dd, 9H, $^2J_{HP} = 9.2$, $^3J_{HP} = 4.5$ Hz), 1.17 (dd, 3H, $^2J_{HP} = 19.1$, $^3J_{HP} = 9.3$ Hz). HRMS-(FAB) Calc.: 585.2122; Found: 585.2107.

4.5. Reaction of **1** with MeI to form DmpP(CH_3)I (**2e**) and [DmpP(CH_3)PMe_3]I (**3e**)

To a solution of **1** (210 mg, 0.500 mmol) in 10 ml THF was syringed 31 μl of MeI (0.500 mmol). After 1 h, the reaction color had changed from an initial bright yellow to a pale yellow and was accompanied with a small amount of white precipitate. A ^{31}P-NMR spectrum of a reaction aliquot showed major resonances at δ 18.2 (d, $J_{PP} = 336$ Hz) and − 36.6 (d, $J_{PP} = 336$ Hz) (**2e**), 49.2 (s) (**3e**), and − 61.4 (s, free PMe_3). In solution, **2e** equilibrates with **3e**. The reaction flask was placed in dry box fridge at − 35°C and after 24 h, white crystalline flakes were filtered, quickly washed with hexanes, and vacuum dried to give 190 mg, presumably of **2e** (yield 67%). The white crystals rapidly equilibrated to give **3f** *and* free PMe_3 when ^{1}H-NMR was attempted in C_6D_6. Addition of PMe_3 to a NMR sample of **3e** in THF gives an equilibrium mixture of **2e** and **3e**. The identity of **3e** was independently confirmed by the addition of either NaI or KI to **2e**. Both reactions also resulted in equilibrium mixtures of **3e** and **2e**.

4.6. Reaction of **1** with Me_3SiI to form DmpP($SiMe_3$)I (**2d**) and [DmpP($SiMe_3$)PMe_3]I (**3d**)

Reaction of **1** and Me_3SiI gives similar reaction mixtures as observed for the reaction of **1** and MeI. ^{31}P-NMR (C_6D_6) δ, 17.0 (d, $J_{PP} = 343$ Hz), − 28.4 (d, $J_{PP} = 343$ Hz) (**2d**) and 65.6 (**3d**).

4.7. Synthesis of DmpP(H)Cl (**3f**)

To a solution of 200 mg (0.476 mmol) of **1** in 20 ml THF at 0°C was added 0.48 ml of a 1.0 M HCl solution (0.480 mmol) in diethyl ether. The initial yellow solution color of **1** faded rapidly to give a pale yellow. After stirring for 3 h, all volatiles were removed under reduced pressure to give a pale yellow–white solid. The solid was dissolved in boiling hexanes and recrystallized at − 35°C to give 103 mg of white crystalline **3f** (57% yield). ^{31}P-NMR ($CDCl_3$) δ 22.2 (d, $J_{PH} = 206$ Hz). ^{1}H-NMR ($CDCl_3$) δ 7.58 (t, 1H, $J_{HH} = 7.8$ Hz), 7.17 (dd, 2H, $^3J_{HH} = 7.6$, $^4J_{HP} = 2.3$ Hz), 6.96 (s, 4H), 5.80 (d, 1H, $J_{HP} = 206$ Hz), 2.35 (s, 6H), 2.05 (s, 6H), 1.96 (s, 6H). HRMS(EI) Calc.: 380.1462; Found: 380.1477.

4.8. Synthesis of DmpP(H)OPh (**3g**)

To a solution of 100 mg (0.238 mmol) of **1** in 5 ml THF was added 22 mg (0.24 mmol) of phenol in 5 ml THF. The initial yellow solution color characteristic of **1** faded to a pale yellow over a period of 15 min. After 15 min of stirring all volatiles were removed under reduced pressure to give 93 mg of pale yellow solid 3g (89%). ^{31}P-NMR ($CDCl_3$) δ 79.7 (d, $J_{PH} = 220$ Hz). ^{1}H-NMR ($CDCl_3$) δ 7.56 (t, 1H, $J_{HH} = 7.7$ Hz), 7.16 (dd, 2H, $J_{HH} = 7.7$, $^4J_{HP} = 2.3$ Hz), 7.01 (m, 2H), 6.95 (s, 2H), 6.84 (m, 1H), 6.80 (s, 2H), 6.48 (m, 2H), 6.38 (d, 1H, $J_{HP} = 221.4$ Hz), 2.31 (s, 6H), 2.10 (s, 6H), 1.90 (s, 6H). HRMS (EI) Calc.: 438.2164; Found: 438.2169.

4.9. Reaction of **1** and H_2O to produce DmpP(O)(H)OH

To 50 mg (0.119 mmol) of **1** in 5 ml THF was syringed in 2.5 μl (0.121 mmol) of degassed deionized water. The initial yellow solution color characteristic of **1** progressively fades and formation of a white precipitate occurs. After 4 h, all volatiles were removed under reduced pressure to afford 41 mg of essentially pure white DmpP(O)H_2 (yield 95%). DmpP(O)H_2 was also independently synthesized using a reported procedure [48]. A mixture of 200 mg (0.580 mmol) of DmpPH_2 and 0.10 ml of H_2O_2 (30% in H_2O, 0.88 mmol) was stirred in 30 ml of EtOH overnight. The solvent was removed and a white powder was obtained (210 mg, 97%). ^{31}P-NMR ($CDCl_3$) δ − 11.5 (t, $J_{HP} = 483$ Hz). ^{1}H-NMR ($CDCl_3$) δ 7.73 (t, $J_{HH} = 7.6$ Hz), 7.22 (dd, 2H, $J_{PH} = 7.6$, $J_{HH} = 3.8$ Hz), 6.96 (s, 4H), 6.85 (d, 2H, $J_{PH} = 483$ Hz), 2.33 (s, 6H), 2.02 (s, 12H). HRMS-EI m/z Calc. for $C_{24}H_{27}PO$: 362.1801; Found: 362.1792.

4.10. X-ray crystallography for **1**

Crystals of **1** were grown from a concentrated hexanes solution at room temperature. Data were collected on a Siemens SMART CCD diffractometer as detailed in Table 1. The structure was solved by direct methods (SHELXS-86) and refined by full-matrix least-squares techniques on F^2 (SHELXL-93). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated at idealized positions and refined at 1.2 times Beq of attached carbon atoms for aromatic carbons and Beq of 1.5 times of attached carbon atoms for methyl groups. The final structure refined to the parameters listed in Table 1. Table 2 lists the resulting bond lengths and angles.

Table 1
Crystal data and structure refinement for **1**

Identification code	jp001
Empirical formula	$C_{27}H_{34}P_2$
Formula weight	420.48
Temperature (K)	203(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions	
a (Å)	16.455(3)
b (Å)	8.542(1)
c (Å)	17.272(3)
α (°)	90
β (°)	93.109(2)
γ (°)	90
V (Å^3)	2424.1(7)
Z	4
D_{calc} (mg m^{-3})	1.152
Absorption coefficient (mm^{-1})	0.190
$F(000)$	904
Crystal size (mm)	$0.10 \times 0.10 \times 0.10$
Theta range for data collection (°)	1.24–22.50
Limiting indices	$-22<h<19$, $-8<k<11$, $-21<l<23$
Reflections collected	10 627
Independent reflections	3164 [$R_{int} = 0.0610$]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameter	3153/0/262
Goodness-of-fit on F^2	1.035
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0577$, $wR_2 = 0.1344$
R indices (all data)	$R_1 = 0.0872$, $wR_2 = 0.1537$
Largest difference peak and hole (e Å^{-3})	0.419 and -0.378

Table 2
Selected bond lengths (Å) and angles (°) for **1**

P(1)–C(1)	1.797(4)	C(1)–P(1)–C(2)	104.0(2)
P(1)–C(2)	1.804(4)	C(1)–P(1)–C(3)	103.2(2)
P(1)–C(3)	1.805(4)	C(2)–P(1)–C(3)	106.7(2)
P(1)–P(2)	2.084(2)	C(1)–P(1)–P(2)	121.5(2)
P(2)–C(9)	1.843(4)	C(2)–P(1)–P(2)	117.4(2)
C(4)–C(5)	1.381(6)	C(3)–P(1)–P(2)	102.3(2)
C(4)–C(9)	1.412(5)	C(9)–P(2)–P(1)	106.79(13)
C(4)–C(16)	1.502(5)	C(5)–C(4)–C(9)	120.3(4)
C(5)–C(6)	1.367(6)	C(5)–C(4)–C(16)	118.3(4)
C(6)–C(7)	1.379(6)	C(9)–C(4)–C(16)	121.3(3)
C(7)–C(8)	1.386(5)	C(6)–C(5)–C(4)	121.4(4)
C(8)–C(9)	1.416(5)	C(5)–C(6)–C(7)	119.1(4)
C(8)–C(24)	1.497(5)	C(6)–C(7)–C(8)	121.9(4)
		C(7)–C(8)–C(9)	119.2(4)
		C(7)–C(8)–C(24)	116.6(3)
		C(9)–C(8)–C(24)	124.2(3)
		C(4)–C(9)–C(8)	118.1(4)
		C(4)–C(9)–P(2)	114.0(3)
		C(8)–C(9)–P(2)	127.5(3)

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 141212 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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