Phosphanylidene-o'-phosphoranes (RP=PR') are phosphorus analogues of alkylidene-o'-phosphoranes (R,C=PR'), better known as Wittig reagents. Phosphanylidene-o'-phosphoranes are synthetically accessible in the free form (RP=PR') and also in the transition-metal-stabilized form (LnM−P(R)=PR').[1] The latter complexes are commonly used in both P=C bond generation and as a source of the phosphinidene (R-P) moiety in the continuing pursuit of new terminal phosphinidene complexes R-P=MLn. In marked contrast, free phosphanylidene-o'-phosphoranes have received little attention because isolable (i.e., thermally stable) examples remain rare.[2–4] Herein we report the synthesis and structure of the stable cyclic phosphanylidene-o'-phosphorane 3 (see Scheme 1). Compound 3 possesses a sterically nonhindered phosphanylidene moiety, yet it is thermally stable enough to be isolated and stored at room temperature. The potential diversity of the coordination chemistry of 3 is illustrated by its transition-metal (Pd0) complex and bis(borane) adduct.

Recently, we synthesized the first “bottleable” (i.e., room temperature stable) phosphine–phosphine donor–acceptor (DA) complex 1.[5] Because of their normally low thermal stability, the reactivity of phosphine–phosphine complexes (other than thermal decomposition pathways) is virtually unknown. Having access to 1, we set off to investigate its chemistry in detail. We were especially intrigued by the possibility of utilizing 1 as a precursor for compounds with a low-coordinate phosphorus atom in the peri position, since no compounds of this type had been reported in the literature.[6] We postulated that the specific peri arrangement of the relatively basic PiPr2 group and the reactive dihalophosphine group should make 1 a good source of “across the peri gap” donor-stabilized, low-valent phosphorus species.

The initial reactivity screen of 1 towards reducing reagents revealed that the reaction with BH3·Me2S proceeded cleanly, giving the bis(borane) adduct 2 (δP = 13.6 and 43.9 ppm, JPP = 198.5 Hz) in almost quantitative yield (Scheme 1). Although 2 does not possess a low-coordinate phosphorus center, the single-crystal X-ray structure (Figure 1)[7] confirmed an interesting bonding situation in which a Lewis-base-stabilized phosphinidene moiety acts as a double donor towards two Lewis-acidic (borane) moieties. Two representative resonance forms of 2 (zwitterionic and with DA bonding) are shown in Scheme 2. The P1/C0–P2/C0 distance in 2 (2.2208(11) Å), is consistent with a P/C=0 single bond. The P2/C0–B1 and P2/C0–B2 distances [1.943(5) and 1.943(4) Å, respectively] are equal and are also as expected for P–B single bonds (typical range 1.90 to 1.95 Å). As mentioned recently by Protasiewicz and co-workers,[2d] whilst of fundamental interest, no bis(borane) push-pull phosphinidene systems have been structurally characterized and compound 2 thus...
removal protocol using dimethylamine was applied to (borane) adduct Me₃P with BH₃·SMe₂.[3d] The (spectroscopically characterized) bis-borane adduct 5a predominantly responsible for the observed increased affinity of the phosphanylidene unit (rather than electronic factors) is (Scheme 1). The notable driving force of the phosphanylidene phosphorane (2,6-Mes₂C₆H₃)-P ars rather acute, and significantly more so than the relevant angle in the only other structurally characterized phosphanylidene phosphorane, 5a failed and only the monoborane adduct 5a·BH₃ was isolated and spectroscopically characterized.[2h-d] Also, Bertrand and co-workers report the only monoborane adduct 6·BH₃ upon reaction of the parent crowded cyclic phosphanylidene-δ-phosphorane 6 with BH₃·SMe₂.[3a] The (spectroscopically characterized) bis-borane adduct Me₆P=PCF₂·2BH₃ thus represents the only other example of a phosphate-donor-stabilized neutral phosphorus atom acting as a double donor to two borane units.[3b] In contrast, several examples of carbene-stabilized phosphorus bis(borane) adducts were reported recently in the literature.[9]

To assess the bonding in the bis(borane) species we calculated the borane dimethyl sulfide (BH₃·SMe₂) addition energies (ΔE_add) to the phosphanylidene phosphoranes 3, 5a, and 6 at the B3LYP-D3 level of density functional theory (Table 1).[9] The notable driving force of ΔE_add = −14.2 kcal mol⁻¹ is computed for the reaction of 3 + 2BH₃·SMe₂, whereas significantly smaller ΔE_add values are obtained for both 5a + 2BH₃·SMe₂ and 6 + 2BH₃·SMe₂ (−6.7 and −6.8 kcal mol⁻¹, respectively). The calculated natural charges (q) on the phosphanylidene P atoms (B3LYP/6-31+G* in the series 3, 5a, and 6 show very little variation from −0.1 (Table 1). It is therefore likely that reduced steric shielding of the phosphanylidene unit (rather than electronic factors) is predominantly responsible for the observed increased affinity of 3 towards borane, and Lewis acids in general. The stability of 2 is indeed remarkable, as it shows no signs of decomposition when stored in air as a solid for weeks at room temperature and only very slow decomposition takes place in wet/oxygenated organic solvents.

To obtain the truly low-coordinate species 3, a borane removal protocol using dimethylamine was applied to 2 (Scheme 1). The phosphanylidene phosphorane 3 was isolated as an intensely red solid in good yield (> 80%). Compound 3 is highly air sensitive, however under inert atmosphere it can be stored without significant signs of decomposition for several weeks even at room temperature. Single-crystal X-ray diffraction confirmed the structure of 3 (Figure 2) with two molecules in the unit cell. The two molecules are almost identical and therefore only one was selected for discussion of the metric parameters. The experimental P1–P2 bond length of 2.148(5) Å is consistent with partial multiple P–P bond character and is significantly shorter than that in 2 (2.2208(11) Å). Indeed the calculated Wiberg bond index (WBI) between the two P atoms in 3 is slightly larger than 1 (Table 1). The P1-P2-C9 angle (90.4(5)) is rather acute, and significantly more so than the relevant angle in the only other structurally characterized phosphanylidene phosphorane, 5a (106.79(13)°). The 31P{1H} NMR spectrum of 3 consists of an AX system with δP = 76.7 (PPh₂) and −157.7 ppm (phosphanylide), with a large magnitude coupling of JPP = 480 Hz. Notably, the chemical shift of the phosphanylidene group in 3 is remarkably dissimilar to that

**Table 1:** Calculated driving force for the addition of 2BH₃·SMe₂, natural charges (q), Wiberg bond indices (WBIs), and optimized parameters for compounds 3, 5a, and 6. Values in parentheses are those for adducts with two BH₃ molecules.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Property</th>
<th>3 (3·2BH₃·2)</th>
<th>5a (5·2BH₃·2)</th>
<th>6 (6·2BH₃·2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔE_add [kcal mol⁻¹]</td>
<td>-14.2</td>
<td>-6.7</td>
<td>-6.8</td>
<td></td>
</tr>
<tr>
<td>q(P)</td>
<td>-0.08</td>
<td>-0.09</td>
<td>-0.09</td>
<td></td>
</tr>
<tr>
<td>q(P_P)</td>
<td>1.25</td>
<td>1.12</td>
<td>1.72</td>
<td></td>
</tr>
<tr>
<td>WBI (P-P) [a]</td>
<td>1.13 (0.94)</td>
<td>1.16 (0.85)</td>
<td>0.92 (0.77)</td>
<td></td>
</tr>
<tr>
<td>P-P-C [°] [b]</td>
<td>89.5</td>
<td>111.5</td>
<td>70.9</td>
<td></td>
</tr>
<tr>
<td>P-P [Å] [c]</td>
<td>2.165 (2.260)</td>
<td>2.141 (2.267)</td>
<td>2.184 (2.289)</td>
<td></td>
</tr>
</tbody>
</table>

[a] Reaction energies (ΔE_add) for X = 2BH₃·SMe₂ → X·2BH₃ + 2SMe₂ (X = 3, 5a, 6), including zero-point and BSSE corrections (B3LYP/6-31+G* level). [b] From NBO analysis, B3LYP/6-31+G* level. [c] B3LYP/6-31+G* level. [d] P_P_P_P_P_C angle.
observed in the four-membered-ring species 6 \( (\delta_P = 58.4 \text{ ppm}) \) \cite{15}, but is only slightly shifted to a lower frequency in comparison to those in 5a \( (\delta_P = -114.7 \text{ ppm}) \) and 5b \( (\delta_P = -134.0 \text{ ppm}) \). A notable shift to a lower frequency is observed in the \(^{31}\text{P} NMR \) spectra upon deprotection of the phosphanylidene \( P \) atom \( (\delta_P = 13.6 \text{ ppm in 2} \) versus \(-157.7 \text{ ppm in 3}) \), and is accompanied by a large increase in the \( J_{PP} \) magnitude (from 198.5 in 2 to 480 Hz in 3)

The \(^{31}\text{P} NMR \) chemical shift of the phosphanylidene atom in 3 appears at a low frequency for a two-coordinate phosphorus. It is more consistent with the ylide resonance structure 3 which features a high electron density phosphorus center having two lone pairs (Scheme 2). The larger contribution of the ylide resonance form 3 is further supported by the observation of an elongated \( P=P \) bond and the WBI value of 1.13 as discussed above, as well as by additional computational methods (see the Supporting Information).

In 1990 Schmidpeter remarked on the importance of the nature of the substituent attached to the phosphanylidene atom for stability of the neutral phosphanylidene phosphoranes, thus stating that in all known species this substituent is either electron withdrawing or bulky. Clearly, incorporation of the phosphanylidene phosphorane moiety into a suitable cyclic system also renders these systems stable. A four-membered-ring skeleton with bulky substituents on the ethylenic moiety is present in the 1,2-diphosphetane 6 (isolated by Bertrand and co-workers), and was shown to have a very persistent \( P=P \) bond. In a similar vein, our phosphanylidene phosphorane 3 consists of a \( \text{C}_2\text{P}_2 \) ring fused to the rigid acenaphthene moiety, with the peri-geometry supporting the \( P=P \) bond. However, it is worth noting that to achieve good thermal stability of cyclic phosphanylidene phosphoranes a correct choice of the ring system and of the substituents is necessary. This is illustrated by an early attempt to make a stable phosphanylidene-\( \alpha \)-phosphorane by the formation of an intramolecular \( P=P \) bond in 7. The strategy, utilizing the formation of a five-membered \( \text{C}_3\text{P}_2 \) ring, was only partially successful and the desired species 7 was observed by \(^{31}\text{P} NMR \) spectroscopy, but decomposed below room temperature.\cite{16}

The reactivity of the free phosphanylidene-\( \alpha \)-phosphorane 3 towards \([\text{Pd}(\text{PHP})]_2\) was examined (Scheme 1). The formation of complex 4 accentuates the phosphine-phosphinidene donor-acceptor aspect of bonding in 3 (see resonance structure 3' in Scheme 2). In this reaction, the palladium(0) center sequestrates the electron density from the phosphine donor (P1) in a molecule of 3. The resulting “deprotected” phosphinidene moiety (P2) readily undergoes dimerization to a diphosphene. All four phosphorus atoms of the newly formed (chelating) ligand are coordinated to Pd\( ^2 \), two as tertiary phosphine donors, and the remaining two as a side-bonded (\( \eta^1 \)) diphosphene. The crystal structure of 4 is shown in Figure 3. The P1–P2 and P3–P4 distances (3.244 and 3.188 Å) indicate there is no bonding interaction across the peri gap in either of the acenaphthene units, whilst the P2–P3 bond length (2.123(4) Å) is consistent with a P=P double bond elongated upon side-coordination to the metal.\cite{17,18,19}

We have shown that the rigid peri-phosphorane molecular scaffold renders stability to the relatively “naked” two-coordinate phosphanylidene center in 3, and represents the first example of a low-coordinate phosphorus center directly at the peri position of acenaphthene. The compound is also the first example of a phosphorus species with (at least partial) multiple bonding between the two peri-atoms. Observation of phosphinidene-like reactivity on coordination of 3 to \( \text{Pd}^0 \) provides additional support for the notation that phosphanylidene phosphoranes can indeed be considered main-group complexes of (i.e., base-stabilized) phosphinides.\cite{20} Our efforts are now directed towards isolation of heavier Group 15 congeners of the species reported herein.

Figure 3. Molecular structure of 4. Thermal ellipsoids are set at 40% probability; hydrogen atoms are omitted for clarity. The (\( i \)) groups on P1 and P4 (two on each) are drawn as wireframe for clarity.

Keywords: density functional calculations · donor-acceptor systems · multiple bonds · phosphorus · structure elucidation


Several (isolable)phosphinophosphanylidene phosphoranes \( R_2P=C=PR_3 \) have been reported from the group of Fritz (see Ref. [1a]), however their chemistry is rather different because of the special nature of the phosphinophosphanylidene group.


CCDC 887823 (2), 887824 (3), and 887825 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Note the widely varying molecular topology (acyclic versus strained cyclic) and large variations in the central \( P_{\text{phosphorane}}-P_{\text{phosphanylidene}}-C \) angles (calculated angles range from 70.9 to 111.5°) in the series 3, 5a, and 6.


The B3LYP-optimized \( P_2-P_3 \) distance is 2.159 Å, the resulting WBI of 1.30 is consistent with substantial double bond character.