

Main Group Chemistry

Adducts of the Parent Boraphosphaketene H_2BPCO and their Decarbonylative Insertion Chemistry

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Abstract: The first examples of Lewis base adducts of the parent boraphosphaketene (H_2B-PCO) and their cyclodimers are prepared. One of these adducts is shown to undergo mild decarbonylation and phosphinidene insertion into a B–C bond of a borole, forming very rare examples of 1,2-phosphaborinines, B/P isosteres of benzene. The strong donor properties of these 1,2-phosphaborinines are confirmed by the synthesis of their π complexes with the Group 6 metals.

Although the 2-phosphaethynolate anion, $[PCO]^-$, has a history stretching back decades or even centuries,^[1,2] it was a series of syntheses of $Na[OCP]$ salts published by Grützmacher and Benkó that provided an accessible nucleophilic reagent for installing the $[PCO]$ unit into organic, main-group and transition-metal systems.^[3] Not surprisingly, considering the parallels with the well-known chemistry of analogous iso(thio)cyanates and the multiple bonding between the P and C atoms in $[XP=C=O]$ (X = organyl or anionic main-group substituent) systems,^[4] these compounds have since shown a wealth of different reactivity patterns, which were summarized in two comprehensive reviews in 2018.^[5] Of these, one of the most fascinating reactivity profiles of phosphaketenes $[XPCO]$ is their propensity for both photolytic and thermal decarbonylation, providing synthetic equivalents of phosphinidenes, $[X-P]$, or in some cases detectable or even isolable variants (Figure 1, top).^[6] This

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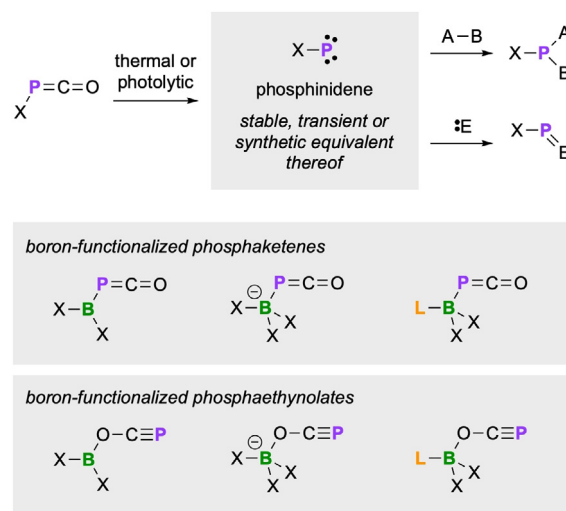


Figure 1. Top: phosphaketenes and their decarbonylation chemistry. Bottom: boron-functionalized phosphaketenes and their phosphaethynolate constitutional isomers.

ability makes phosphaketenes excellent reagents for forming both single and multiple phosphorus–element bonds.^[6,7]

The generation of the first boron-functionalized phosphaethynolates was reported in 2017, but their definitive isolation and structural confirmation was provided by Goicoechea and co-workers in 2018.^[8] Thus far only a handful of boron-functionalized phosphaethynolates/phosphaketenes (i.e. $[X_2B-PCO]$, $[LX_2B-PCO]$ (L = neutral Lewis donor), $[X_3B-PCO]^-$ or their alternative OCP isomers; Figure 1, bottom) have been reported, however, they have already shown a range of interesting reactivities. A number of reactions in which boron-functionalized phosphaethynolates act as synthetic equivalents for phosphinidenes have recently been reported by the groups of Goicoechea and Gilliard, including: a) exchange of CO at the X_2BPCO unit by $CNtBu$,^[8d] b) decarbonylation and formal phosphinidene dimerization,^[8d] and c) intramolecular phosphinidene insertion of a $[PCO]$ -substituted borafluorene.^[8c] However, these are the only demonstrated phosphinidene-like reactivity patterns of boraphosphaketenes, with cyclization, rearrangement and carboboration processes otherwise dominating the reported chemistry of these species.^[8]

We envisaged that the connection of the phosphaethynolate ($[PCO]^-$) anion to cyclic alkyl(amino)carbene (CAAC^[9])-stabilized borenium fragment, $[(CAAC)BH_2]^+$, likely forming an adduct of the parent boraphosphaketene $[H_2BPCO]$, would create an intriguing situation whereby the

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boron-bound hydrogens could potentially migrate to the CAAC carbon atom,^[10] the phosphorus, or even the sp-hybridized carbon atom of the [PCO] unit. Loss of CO from any of these molecules could provide a number of products, including a CAAC adduct of the parent phosphinoborane (i.e. [(CAAC)(H)B=PH]) or a phosphinidene of the form [(CAAC)H₂B=P]. Herein, we present the synthesis of two CAAC adducts of the parent boraphosphaketene [H₂BPCO], their dimerization and intermolecular phosphinidene insertion chemistry to form P-functionalized 1,2-phosphaborinines (BP isosteres of benzene), and the coordination of these heterocycles to transition metals. The results highlight the excellent potential of the [PCO] unit to act as a source of phosphinidenes for the construction of novel heterocycles, in addition to providing access to the first metal complexes of phosphaborinines.

In initial work, the CAAC-stabilized triflatoboranes [(CAAC^R)BH₂(OTf)] (CAAC^R = CAAC^{Me} (**1a**), CAAC^{Cy} (**1b**); see Figure 2) were found to be excellent substrates for the nucleophilic addition of the sodium phosphoethynolate anion, with high conversion observed at room temperature after one hour to species with high-field ³¹P NMR resonances (**2a**: −337 ppm; **2b**: −339 ppm; Figure 2).^[11] However, the initial products, presumed to be the boraphosphaketenes [(CAAC^R)BH₂(PCO)] (CAAC^R = CAAC^{Me} (**2a**), CAAC^{Cy} (**2b**)), were both found to be unstable in solution, converting over time to species with ³¹P NMR spectroscopic resonances at ca. δ_P = 125 (**3a,b**). While all attempts to isolate **2b** as a solid sample led only to the isolation of **3b**, **2a** was obtained

as a yellow solid in 81 % yield. Unfortunately, all attempts to grow crystallographic-quality single crystals of **2a**, even at −30 °C, provided only samples of its conversion product **3a**, precluding the structural determination of the former.

The ³¹P NMR resonance of **2a** (δ_P = −337) is close to that reported by Goicoechea and co-workers for a boraphosphoethynolate (i.e. BOCP; δ_P = −286),^[8c] and a compound of Wilson and Gilliard that was assigned as a boraphosphaketene on the basis of crystallographic data (BPCO; δ_P = −290).^[8d] However, a strong, metal-carbonyl-like band observed at 1899 cm^{−1} in the IR spectrum of **2a** suggested that the compound is indeed the boraphosphaketene isomer. Such a band is absent in the IR spectrum of Goicoechea's boraphosphoethynolate,^[8c] while no IR spectrum was reported for the compound of Wilson and Gilliard.^[8d] The doublet ¹³C{¹H} NMR resonance for the P-bound carbon nucleus provided further evidence for the [BPCO] connectivity of **2a**, with its chemical shift and ¹J_{PC} coupling constant (δ_C = 192.8; ¹J_{PC} = 44.4 Hz) far better resembling that of the Gilliard and Wilson boraphosphaketene (δ_C = 192.0; ¹J_{PC} = 80.4 Hz) than that of Goicoechea's boraphosphoethynolate (δ_C = 140.2; ¹J_{PC} = 17.6 Hz). The [BPCO] connectivity of **2a** is also supported by DFT calculations, with computed δ_C, δ_B and δ_P chemical shifts of 202, −32 and −338 (exp: 192.8, −27.3, −337), respectively, and a metal-carbonyl-like vibrational frequency at 1950 cm^{−1} (exp. 1899 cm^{−1}). In contrast, the corresponding calculated chemical shifts for the [BOCP] isomer are 166, −6, and −320, while the metal-CO vibrational frequency was predicted to be 1697 cm^{−1}.

The conversion product **3a** was obtained in 73 % yield by storing a solution of **2a** at −30 °C for two weeks, while **3b** was obtained in 84 % yield by drying, washing and crystallizing a mixture of **1b** and Na[OCP]. Compounds **3a,b** were confirmed to be the *cyclo*-C₂P₂ dimers of the monomeric boraphosphaketenes **2a,b** by single-crystal X-ray diffraction (SCXRD; Figure 2, bottom). The C₂P₂ cores of **3a,b** are essentially isostructural with that of their most comparable reported structure, a dimer of an organyl phosphaketene, [OCPC(*p*-C₆H₄OMe)₃]₂, from Benkó and Grützmacher.^[3b] Only slight differences in the pyramidalization at the P atoms were noted (Σ_P **3a**: 299.2°; **3b**: 306.0°; [OCPC(*p*-C₆H₄OMe)₃]₂: 308.3°), with the greatest pyramidalization being observed in the least sterically hindered example, **3a**. The dimerization of **2a,b** through their P=C bonds, forming cycles with B–P–C=O connectivity, is further evidence for the boraphosphaketene structures of the former. Further heating of **3a,b** (60 °C for 8 h) led to their complete consumption but ultimately provided only intractable mixtures, from which only the corresponding CAAC–BH₃ adduct could be identified.

Having the new boraphosphaketene **2a** in hand as a stable, isolated solid, we sought to explore its phosphinidene-generating abilities. Although photolysis of **2a** led only to intractable mixtures of unidentifiable compounds, the 1:1 molar reactions of **2a** with boroles provided much more promising results. In 2015, Martin and co-workers reported the synthesis of the first 1,2-phosphaborinines, BP isosteres of benzene, by formal insertion of a phosphinidene derived from *cyclo*-[P₅Ph₅] into boroles.^[12] In our hands, combining phos-

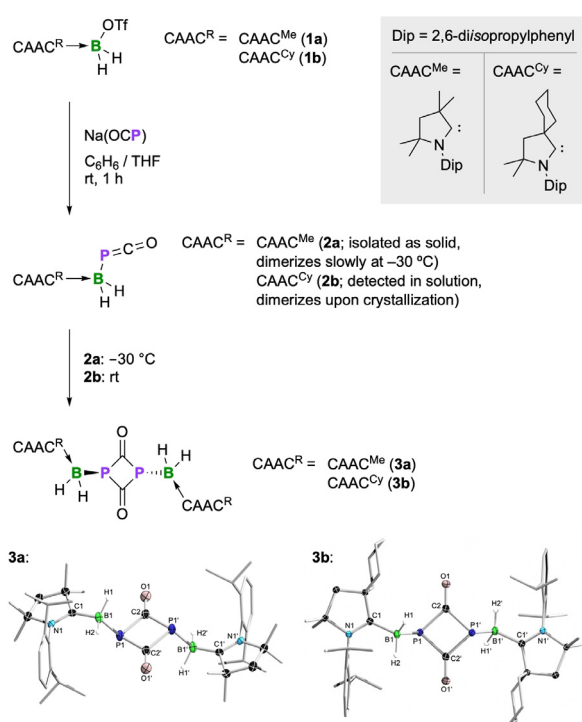


Figure 2. Top: generation of CAAC-stabilized boraphosphaketenes **2a,b** and their dimers **3a,b**. Bottom: crystallographically determined solid-state structures of **3a,b**.^[21] Ellipsoids shown at the 50% probability level. Ellipsoids of peripheral groups and all hydrogen atoms except those attached to boron have been removed for clarity.

phaketene **2a** with boroles [RBC₄Ph₄] (R = Ph, 2-thienyl, Mes) at room temperature led to the decarbonylative insertion of the phosphinidene [(CAAC^{Me})(H)₂B–P] into the borole ring and isolation of yellow solids **4a–c** in good yields (86–93%; Figure 3). The 1,2-phosphaborinines **4a–c** show moderate deviation in the ¹¹B and ³¹P NMR resonances of their endocyclic heteronuclei (**4a**: $\delta_B = 42.8$, $\delta_P = 81.0$; **4b**: $\delta_B = 39.7$, $\delta_P = 80.4$; **4c**: $\delta_B = 45.7$, $\delta_P = 72.1$), these data being in line with those of the only other known phosphaborinines (the exocyclic boron nuclei (**4a**: $\delta_B = -28.0$; **4b**: $\delta_B = -27.9$; **4c**: $\delta_B = -28.1$), which are more distant from the varying R group. Disorder present in the central C₄BP ring of the solid-state structure of **4a** prevents detailed analysis of the endocyclic metrical parameters, but unambiguously confirmed the identity of the 1,2-phosphaborinine **4a** (see Figure 3). **4a** displays a planar C₄BP unit with five phenyl groups oriented in a propeller-like fashion, as frequently observed for their BN homologues, 1,2-azaborinines.^[13]

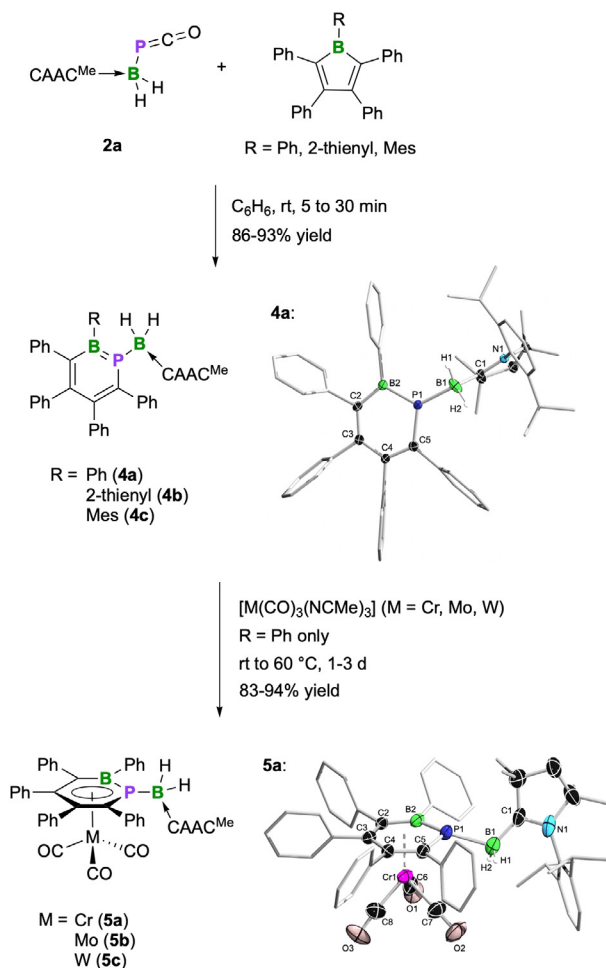


Figure 3. Synthesis of borylated phosphaborinines **4a–c** and π complexes of **4a** with group 6 transition metals (**5a–c**). Insets at right: crystallographically determined solid-state structures of **4a** and **5a**.^[21] Ellipsoids shown at the 50% probability level. Ellipsoids of peripheral groups and all hydrogen atoms except those attached to boron have been removed for clarity.

As mentioned above, Wilson and Gilliard et al. reported the formal intramolecular insertion of a PCO-derived phosphinidene into a borafuorene, an aryl-fused borole.^[8d] However, the syntheses of 1,2-phosphaborinines **4a–c** are noteworthy in their intermolecular nature, as well as the fact that all reports of intermolecular reactions of boroles with isocyanates and isothiocyanates (analogs of phosphaketenes) have resulted in the insertion of the N=C or C=O bond into the borole ring rather than decarbonylation.^[14] It should also be noted that the room-temperature reaction of the P₂C₂ dimer **3a** with pentaphenylborole did not lead to the 1,2-phosphaborinine **4a**. This result highlights the unique reactivity of boraphosphaketene **2a** and suggests the irreversibility of the dimerization process of **2a,b** to **3a,b**.

The electronic structure and the aromatic nature of the 1,2-phosphaborinine **4a** were investigated theoretically by DFT calculations. The frontier molecular orbitals are depicted in Figure 4a. The HOMO is π -delocalized through the central C₄BP ring, and exhibits π bonding character in the boron–phosphorus region. On the other hand, the LUMO is mainly composed of the C–N π^* orbital at the CAAC ligand. A large HOMO–LUMO gap of ca. 4 eV is found, in line with the high kinetic stability observed for the system. The anisotropy of the induced current density (ACID) plot,^[15] shown in Figure 4b, displays clockwise diatropic ring current flow in the central ring, which is indicative of aromatic character. This picture is corroborated by nucleus-independent chemical shift (NICS) calculations.^[16] The scan of the

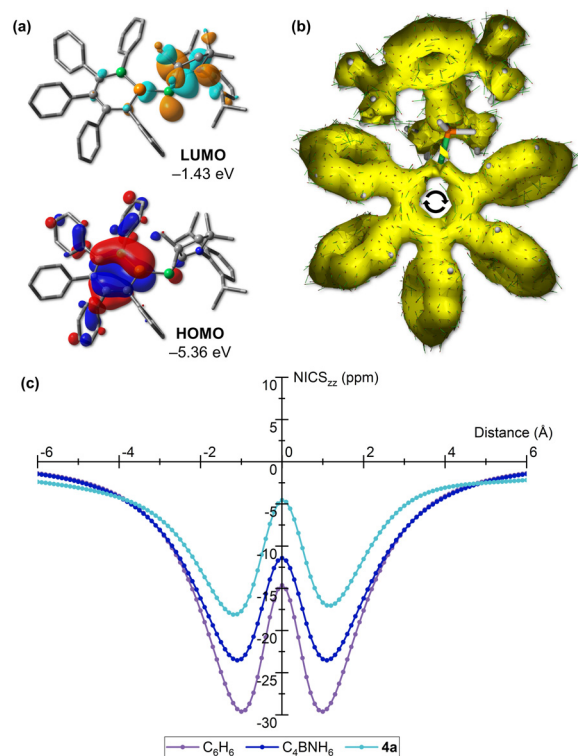


Figure 4. a) Canonical Kohn–Sham molecular orbitals (MOs) of **4a** at the PBE0-D3(BJ)/6-31+G** level; b) calculated ACID plot (isovalue: 0.025) of **4a**; c) NICS_{zz} scan curves of C₆H₆, C₄BNH₆ and **4a** at the PBE0-D3(BJ)/6-311++G** level.

NICS_{zz} component at points along the axis perpendicular to the ring plane above and below the ring is shown in Figure 4c. Similarly to benzene and to the parent 1,2-azaborinine C₄B₂NH₆, the NICS_{zz} scan of **4a** also displays a minimum value in the negative NICS_{zz} region. The computed NICS(0) and NICS_{zz}(1) values of **4a** are −5.48 ppm and −16.70 ppm, respectively. These values are less negative than those obtained for benzene (NICS(0) = −8.24 ppm; NICS_{zz}(1) = −29.62 ppm) and C₄B₂NH₆ (NICS_{zz}(1) = −6.81 ppm; NICS_{zz}(1) = −22.45 ppm), and are similar to those of Martin's 1,2-phosphaborinine systems.^[12] Together with the planarity of the central ring, these results indicate that **4a** features a moderate degree of aromaticity.

In order to probe the ability of 1,2-phosphaborinine **4a** to coordinate to transition metals, it was treated with group 6 complexes [M(CO)₃(NCMe)₃] (M = Cr, Mo, W). The reaction mixtures were monitored in situ by ¹¹B and ³¹P NMR spectroscopy, which showed full consumption of **4a** after one to three days at room temperature or 60 °C, respectively. The half-sandwich complexes **5a–c** were isolated as yellow solids in good to excellent yields (83–94 %). The ¹¹B NMR resonances of the endocyclic boron nuclei were upfield-shifted ca. 16 ppm (**5a**: δ_B = 27.5; **5b**: δ_B = 27.1; **5c**: δ_B = 25.2) compared to that of non-coordinated **4a**, which is in accordance with the reported change of the chemical shift of a 1,2-thiaborinine upon coordination to [Cr(CO)₃].^[17] The significant upfield shift of the ³¹P NMR signal (**5a**: δ_P = −12.6; **5b**: δ_P = −4.59; **5c**: δ_P = −21.3) suggests that the coordination of the central C₄BP ring to the metal involves the respective phosphorus atoms.

An X-ray crystallographic analysis of **5a** confirmed the η⁶-coordination of the C₄BP core with a centroid...Cr1 distance of 1.709 Å between the planar 1,2-phosphaborinine ring and the Cr center. The phosphorus atom is slightly pyramidalized (ΣP1 = 354.8(2)°), with the exocyclic BH₂ unit bent towards the Cr center. Solid-state IR spectroscopy performed on complexes **5a–c** revealed sets of C–O stretching bands (**5a**: ν̄(CO) = 1936, 1872, 1850 cm^{−1}; **5b**: ν̄(CO) = 1943, 1855 cm^{−1}; **5c**: ν̄(CO) = 1936, 1870, 1845 cm^{−1}) that are significantly lower in frequency than those of Martin's thiaborinine–Cr(CO)₃ complex (ν̄(CO) = 1964, 1908, 1873 cm^{−1}) as well as those of a 1,2-azaborinine chromium complex (ν̄(CO) = 1979, 1916, 1900 cm^{−1}) reported by Ashe,^[17,18] implying much stronger backdonation from the 1,2-phosphaborinine–metal fragment into the π* orbitals of the CO ligands. The remarkable donor ability of **4a** was corroborated experimentally by heating C₆H₆ solutions of **5a–c** at 80 °C over a period of one week, which, in contrast to Martin's thiaborinine–Cr(CO)₃ complex, showed no signs of decomposition.^[17]

The complexation energies of **4a** with the [M(CO)₃] (M = Cr, Mo, W) fragment (thus forming complexes **5a–c**) were analyzed computationally by decomposing the total energy ΔE into strain and interaction contributions (ΔE = ΔE_{strain} + ΔE_{int}, see SI for details).^[19] For comparison, we also computed the complex [(η⁶-C₆H₆)Cr(CO)₃]. The complexation energy obtained for the latter system was −69.5 kcal mol^{−1}, where a small ΔE_{strain} contribution of +3.8 kcal mol^{−1}, which arises mainly from structural distortions of the benzene ligand, slightly reduces the strong ΔE_{int} value of −73.3 kcal mol^{−1}.

These results are in good agreement with previous theoretical studies.^[20] In turn, the complexation energies of the [4a-M(CO)₃] systems are significantly larger than that of [(η⁶-C₆H₆)Cr(CO)₃], being −85.6, −82.2 and −98.8 kcal mol^{−1} for M = Cr, Mo and W, respectively. Although in these cases the ΔE_{strain} can reach values as high as +15.7 kcal mol^{−1}, the strong ΔE_{int} contributions dictate the more stabilizing role of the **4a** ring with respect to benzene.

In this work we have prepared the first examples of adducts of the parent boraphosphaketene (H₂B–PCO) and documented their tendency towards dimerization to form compounds with four-membered C₂P₂ cycles. We have also demonstrated the ability of a boraphosphaketene adduct to undergo mild decarbonylation and phosphinidene insertion into a B–C bond of a range of boroles, forming B/P heterocyclic compounds. The strong donor properties of these 1,2-phosphaborinines are confirmed by the synthesis of their π complexes with the Group 6 metals. Overall, we hope this work will stand as a demonstration of the synthetic power of boron-bound phosphaketenes as reagents for forming new classes of compounds by the formation of single and double phosphorus–element bonds.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: boron · decarbonylation · heterocycles · ketenes · phosphorus

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