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Hydroboration of Phosphaalkynes by $\text{HB}(\text{C}_6\text{F}_5)_2$ Lauren E. Longobardi,^[a] Timothy C. Johnstone,^[a] Rosalyn L. Falconer,^[b] Christopher A. Russell,^[b] and Douglas W. Stephan^{*[a]}

Abstract: The hydroboration of phosphaalkynes with Piers' borane ($\text{HB}(\text{C}_6\text{F}_5)_2$) generates unusual phosphaalkenylboranes $[\text{RCH}=\text{PB}(\text{C}_6\text{F}_5)_2]_2$ that persist as dimers in solution and the solid state. These P_2B_2 heterocycles undergo ring opening when subjected to nucleophiles, such as pyridine and *tert*-butylisocyanide, to yield monomeric phosphaalkenylborane adducts $\text{RCH}=\text{PB}(\text{C}_6\text{F}_5)_2(\text{L})$. DFT calculations were performed to probe the nature of the interaction of phosphaalkynes with boranes.

Hydroboration is a powerful chemical transformation in which B–H bonds are added across unsaturated units in alkynes, olefins, imines, and carbonyl compounds.^[1] These additions are typically facilitated by transition metal catalysts.^[2] The widespread utility of this chemical reaction in organic synthesis has been realized since the initial work by H.C. Brown in the 1960s.^[3] Although related chemistry has been achieved to exploit the utility of carbaborations^[4] and haloborations,^[5] more recent innovations have included the development of metal-free catalysts for hydroboration and the specific design of borenium catalysts for *trans*-hydroborations of alkynes.^[6] Despite the broad utility of hydroboration in organic chemistry, exploitation of this reaction in main group inorganic chemistry has drawn little attention.

The isolation of stable, singlet P_2B_2 diradicaloids by Bertrand and co-workers^[7] and the advent of frustrated Lewis pairs (FLPs),^[8] are two examples of chemistry that has focused attention on compounds containing phosphorus and boron. In seeking to exploit hydroboration for the preparation of novel P/B compounds, we noted that low-coordinate phosphorus species such as phosphaalkenes^[9] and phosphaalkynes,^[10] have a rich and diverse reactivity but few examples of boron-containing derivatives exist.^[11] Phosphaalkynes have been reported to react with BBr_3 to yield 1,2-addition products (Figure 1 **A**),^[12] and also polyhedral boranes, resulting in either linkage of B_{10} units by phosphaalkene fragments^[13] or incorporation of the $\text{P}\equiv\text{C}$ fragment into the polyhedral cluster.^[14] Phosphaalkynes have also been shown to insert into boroles^[15] and a Ti-phosphaalkyne complex was observed to undergo addition of HBEt_2 to afford a unique P/B-Ti complex (Figure 1, **B**).^[16]

Aside from Ti species **B**, the direct addition of an $\text{R}_2\text{B-H}$ bond to a phosphaalkyne has been reported only once, to the best of our knowledge. In that case, the double hydroboration of *tert*-butylphosphaalkyne ($t\text{BuC}\equiv\text{P}$ **1a**) with HBCat (Cat = catechol) generated a *gem*-diboryl substituted primary phosphine (Figure 1, **C**).^[17] The regiochemistry of this 1,2-addition reaction is governed by the electronegativity difference between carbon and phosphorus and the inherent polarity of the $\delta^+\text{P}\equiv\text{C}\delta^-$ bond. This regiochemistry of 1,2-addition has also been observed in related hydrogermylation^[18] and hydrostannation chemistry.^[19] In contrast, the aforementioned reaction of HBEt_2 with a Ti-phosphaalkyne complex resulted in B–P bond formation.^[16] Although this reaction does not involve B–H addition to the $\text{P}\equiv\text{C}$ bond, it suggests that steric demands might also play a role in determining the regiochemistry of phosphaalkyne addition reactions. Herein we report the reaction of phosphaalkynes with the highly electrophilic borane $\text{HB}(\text{C}_6\text{F}_5)_2$,^[20] which affords the first examples of simple B–P bonded phosphaalkenylboranes and a novel class of P/B heterocycles.

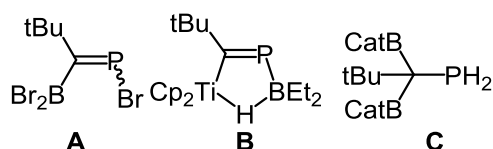


Figure 1 Reported products arising from reactions between phosphaalkynes and boranes.

To study the reactivity of phosphaalkynes with highly electrophilic boranes, **1a** was exposed to one equivalent of the strong Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$. Multinuclear NMR spectroscopy showed no evidence of coordination or carboboration^[4c] even after prolonged heating, in contrast to the reactivity of $\text{B}(\text{C}_6\text{F}_5)_3$ with alkynes. We attribute the lack of interaction to the low basicity and nucleophilicity of the P-centre.^[21] Similarly, treatment of **1a** with $\text{B}(\text{C}_6\text{F}_5)_3/\text{PtBu}_3$ or $\text{B}(\text{C}_6\text{F}_5)_3/\text{PPH}_3$ at ambient or elevated temperatures showed no addition across the $\text{P}\equiv\text{C}$ bond, in contrast to the reported reactivity of frustrated Lewis pairs (FLPs) with $\text{C}\equiv\text{C}$ bonds.^[22] Treatment of **1a** with one equivalent of Piers' borane ($\text{HB}(\text{C}_6\text{F}_5)_2$)^[20] in CH_2Cl_2 , however, afforded a colourless crystalline solid **2a** in 67% yield after workup (Scheme 1). Single crystals for X-ray diffraction were obtained via diffusion of pentane into a CH_2Cl_2 solution of **2a** at -35°C (Figure 2a). The solid state structure revealed that hydroboration of the phosphaalkyne had occurred and produced a phosphaalkenylborane, which dimerized to form a P_2B_2 four-membered ring.^[23] The phosphaalkene $\text{P}=\text{C}$ bond lengths were 1.651(2) and 1.6470(19) Å. The P_2B_2 ring is distorted from planarity in a butterfly conformation featuring a dihedral angle of $23.32(8)^\circ$. P–B–P bond

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angles of 81.14(8)° and 81.01(8)°, and B–P–B bond angles of 96.17(9)° and 96.24(9)° were found in the central ring. The P–B bond lengths in **2a** ranged from 2.009(2) – 2.013(2) Å; these distances are at the short end of those of phosphinoborane dimers, [R₂B–PR'₂]₂, which range from 2.004(4) to 2.096(5) Å,^[24] but are longer than those of P₂B₂ diradicaloids, which range from 1.8904(15) to 1.900(2) Å.^[7] The short P–B distances in **2a** are perhaps due to the reduced steric demands of the bridging phosphalkene units or the hybridization of the P-centre.

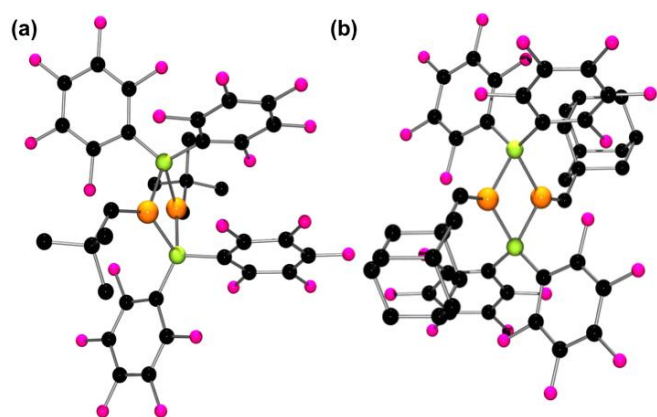
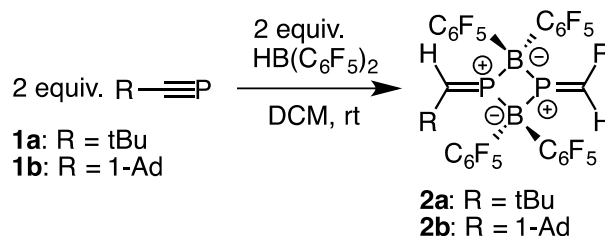


Figure 2 POV-ray depictions of (a) **2a** and (b) **2b**. H atoms omitted for clarity. C: black, B: yellow-green, F: pink, P: orange.

The ¹¹B NMR spectrum of **2a** revealed a sharp singlet at -5.3 ppm and the ¹⁹F NMR spectrum showed three resonances at -127, -153, and -162 ppm. These data support the assignment of **2a** as a four-coordinate boron species, consistent with a dimer in solution. ³¹P NMR data revealed a broad singlet at 183 ppm, a drastic downfield change in chemical shift from that of phosphalkyne **1a** (-69 ppm)^[11a], consistent with the formation of a phosphalkene. The ¹H NMR spectrum showed two resonances at 8.03 and 1.04 ppm, with relative integrations of 1:9, which were assigned as the olefinic and *t*Bu resonances, respectively. Surprisingly, the resonance at 8.03 ppm appears as a triplet with an apparent coupling constant of *J* = 8.2 Hz. The triplet resonance persists even when recorded at differing magnetic field strengths and temperatures (25 to -35 °C). The ¹H{³¹P} spectrum, however, reveals this resonance as a singlet, indicating that the fine structure of the signal arose from coupling between the H and P nuclei. ¹³C{¹H} NMR data showed resonances at 178, 41, and 30 ppm, all of which were apparent triplets. The multiplicity of the ¹H and ¹³C NMR signals appears to arise from virtual coupling to the pair of strongly coupled ³¹P nuclei in **2a**. The two putatively coupled phosphorus centres in **2a** have identical chemical shifts in solution and thus do not exhibit any coupling to each other. A similar phenomenon has been observed for *trans*-diphosphine metal complexes,^[25] and the structurally analogous dimeric four-membered heterocycle [LiPPh₂]₂.^[26] Further confirmation of this interpretation is derived from ssNMR data. Fortuitously, dimer **2a** sits on a general position in the solid state and thus the two P-centres are crystallographically inequivalent. Consequently, the CP-MAS ssNMR ³¹P{¹H} spectrum of **2a** (Figure S33) exhibits two ³¹P resonances that couple to each other with ²*J*_{bp} ~ 1520 Hz. Simulation of the solution state ¹H NMR resonance of the olefinic proton of **2a** as an ABX multiplet using 1520 Hz as *J*_{AB} suggests

that the coupling between the two phosphorus centres is sufficiently large to collapse the second order ABX multiplet into an apparent triplet (Figure S34).

Given the difference in the electronegativities of carbon and phosphorus, and the polar nature of the P≡C bond, it is interesting to note that the hydroboration occurs with formation of P–B and C–H bonds. This pattern of reactivity stands in contrast to literature reports of B–H,^[17] Ge–H,^[18] and Sn–H^[19] phosphalkyne addition reactions, in which hydride adds to the more electropositive phosphorus affording a P–H bond. Interestingly, the formation of **2a** is more akin to reactions of phosphalkynes with Ru–H species described by Hill, Jones^[27] and Crossley,^[28] reinforcing the analogy between electrophilic boranes and transition metals. We also noted that, unlike the previously reported double addition of HBCat to phosphalkyne,^[17] Piers' borane undergoes a single 1,2-addition to **1a**, and any excess borane remains unreacted in solution, as evidenced by multinuclear NMR spectroscopy.



Scheme 1. Reactions of phosphalkynes **1a/b** with HB(C₆F₅)₂ to produce **2a/b**.

To probe the mechanism of reaction and the observed regiochemistry in the formation of **2a**, DFT computations were performed. Inspection of the *f*₁(*r*) Fukui function clearly reveals that the site of electrophilic attack is the P≡C triple bond, and not the lone pair on the phosphorus atom (Figure S36). This view is in accord with the partial positive charge on the phosphorus atom resulting from the difference in electronegativity between phosphorus and carbon. Relaxed potential energy surface (PES) scans of the distance between the centre of the P≡C triple bond and the boron atom of either Piers' borane or B(C₆F₅)₃ were performed. These surface scans reveal that the energy of the system experiences a minimum as Piers' borane approaches the triple bond. In contrast, the energy monotonically rises as B(C₆F₅)₃ and phosphalkyne approach one another (Figure S35). The latter result suggests that steric repulsion between the C₆F₅ rings and the *tert*-butyl group precludes approach of B(C₆F₅)₃ and the nucleophilic π cloud of the phosphalkyne. The minimum from the PES scan with Piers' borane was used as the starting point for a geometry optimization. In the optimized configuration, the BH is directed towards the carbon atom of the phosphalkyne (Figure 3). This configuration is favourable as it minimizes steric interactions between the C₆F₅ rings and the *tert*-butyl group. These results are congruent with chemical intuition and account for the lack of reactivity with B(C₆F₅)₃ and the observed regiochemistry of the reaction with Piers' borane.

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The analogous reaction of 1-adamantylphosphaalkyne (1-AdC≡P **1b**) with Piers' borane resulted in formation of the dimeric species **2b** in 68% yield (Scheme 1). Compound **2b** also shows virtual coupling of the P-atoms to ^1H and ^{13}C nuclei in solution state NMR spectra. However, unlike **2a**, the P_2B_2 unit of **2b** is centrosymmetric in the solid state (Figure 2b), with B–P distances of 2.021(3) and 2.023(4) Å. The B–P–B and P–B–P angles were found to be $98.5(1)^\circ$ and $81.5(1)^\circ$, respectively, and the P=C double bond length is 1.649(3) Å, similar to that of **2a**.

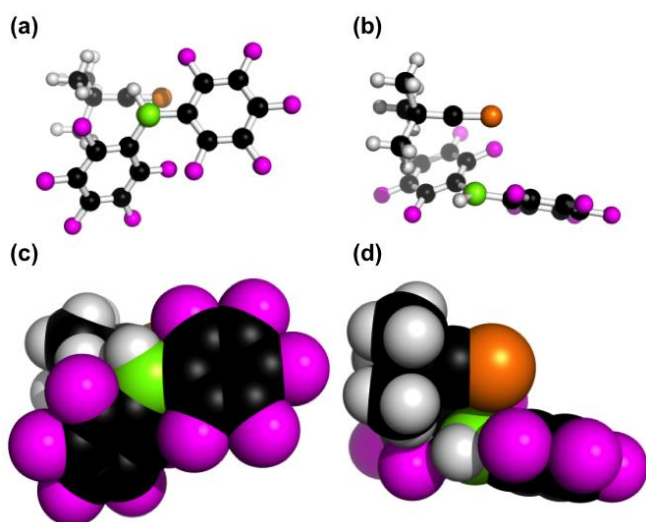
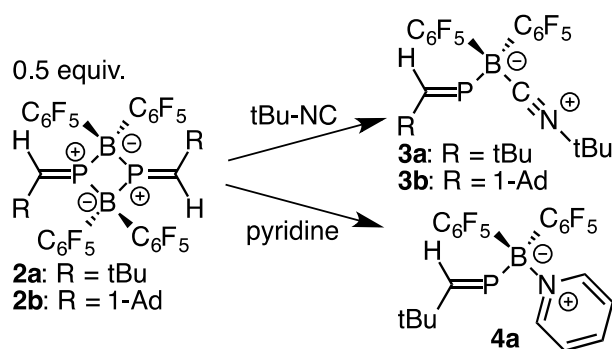


Figure 3. Ball-and-stick (a and b) and space-filling (c and d) depictions of the optimized geometry of Piers' borane approaching **1a** viewed from top (left) and side (right). H: white, C: black, B: yellow-green, F: pink, P: orange.

Investigations of the reactivity of dimers **2a/b** revealed their thermal instability. Both decompose in $\text{C}_6\text{D}_5\text{Br}$ with modest heat (60°C) or upon standing at room temperature in halogenated solvents over several hours. Given the short P–B bond lengths and the strong NMR spectroscopic coupling observed in **2a/b**, we anticipated the dimers to be unreactive towards small molecules. Indeed, **2a** shows no reactivity with H_2 , CO_2 , or CO . Upon treatment with *tert*-butylisocyanide, however, a rapid and clean reaction occurred, affording a new species **3a**, which we propose to be the monomeric phosphoalkenylborane adduct (Scheme 2). This assignment was supported by loss of the ^1H NMR virtual triplet of **2a**, and the appearance of a doublet at 8.75 ppm with $J = 24$ Hz. Compound **3a** gives rise to a ^{19}F NMR spectrum comprising three resonances at -130, -157, and -163 ppm, while the ^{11}B NMR resonance appears at -22 ppm. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum features a pentet at 266 ppm, with $J = 36$ Hz, while in the $^{31}\text{P}\{^{19}\text{F}\}$ spectrum, the resonance collapsed to a doublet with $J = 24$ Hz. This evidence suggests that the phosphorus centre couples to both the olefinic proton and the four *ortho*-fluorines of the two C_6F_5 rings. This reactivity contrasts with that of phosphinoborane dimers $[(\text{C}_6\text{F}_5)_2\text{BPR}_2]_2$ which proved unreactive toward donor molecules.^[24, 29] Collectively these data are consistent with the formulation of **3a** as $t\text{BuCH}=\text{PB}(\text{C}_6\text{F}_5)_2(t\text{BuNC})$.

Scheme 2. Reactions of dimers **2a/b** with *tert*-butylisocyanide and pyridine to produce **3a/b** and **4a**, respectively.



The adduct **3a** was consistently isolated as a pale oil, so analogous chemistry with **2b** was undertaken with the goal of obtaining crystallographic data. Compound **2b** also reacted cleanly with *tert*-butylisocyanide, affording (1-Ad)CH=PB(C_6F_5)₂(*t*BuNC) **3b**, which was confirmed crystallographically. Additionally, when **2a** was treated with pyridine, the resulting adduct $t\text{BuCH}=\text{PB}(\text{C}_6\text{F}_5)_2(\text{pyr})$ **4a** could be isolated as a crystalline material (Scheme 2). Species **3b** exhibits solution NMR spectra with similar properties to those of **3a**, while **4a** has a ^{11}B NMR resonance at -0.8 ppm. X-ray data for both **3b** and **4a** confirmed the formulations (Figure 4). For both molecules, the B-centre adopts a pseudo-tetrahedral geometry. The average B–C_{isocyanide} bond distance of **3b** is 1.61(1) Å, and the B–N bond distance of **4a** is 1.612(3) Å. The P–B bond lengths average 2.040(7) Å in **3b** and was found to be 2.029(2) Å in **4a**. These P–B distances are significantly longer than those of $(\text{C}_6\text{F}_5)_2\text{BPR}_2$ (R = *t*Bu, Cy),^[24] which were found to be 1.786(4) Å and 1.762(4) Å. This difference presumably reflects the poorer sigma-donor ability of sp^2 vs sp^3 phosphorus. The P=C bond lengths average 1.657(6) Å in **3b** and 1.669(2) Å in **4a** with B–P–C average angles of $103.7(3)^\circ$ and $105.1(1)^\circ$, respectively. These P=C bond lengths fall within the range typically observed for phosphoalkenes (1.661(6)–1.690(2) Å).^[18, 30] These represent the first examples of phosphoalkenylboranes to be synthesized, and crystallographically characterized.

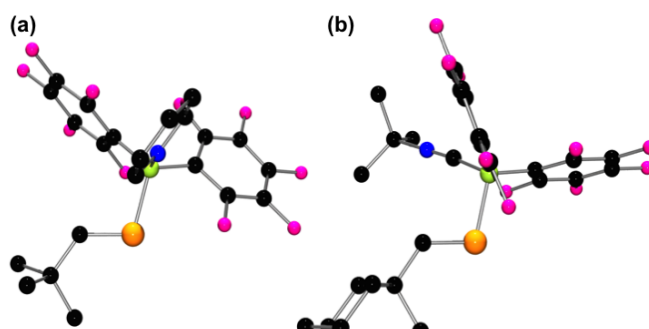


Figure 4. POV-ray depiction of (a) **4a** and (b) **3b**. H atoms omitted for clarity. C: black, B: yellow-green, F: pink, N: blue, P: orange.

In summary, hydroboration of phosphoalkynes with Piers' borane proceeds with an unexpected regiochemical outcome to give phosphoalkenylboranes, which are dimeric in the solid and solution state. Despite their apparently short P–B bonds, the P_2B_2

rings of these compounds were readily cleaved in the presence of donors, affording monomeric phosphalkenylborane adducts. The products **2**, **3**, and **4** are unique examples of phosphalkenes and illustrate the impact of electrophilic acceptors on the regiochemistry of the hydroboration of phosphalkynes. This is a motif that has, to the best of our knowledge, not yet been reported. Efforts to study these unusual P/B systems and exploit their reactivity are ongoing.

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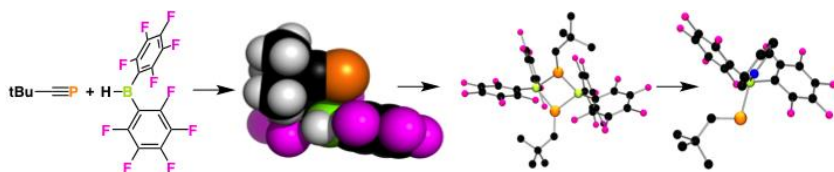
Keywords: hydroboration • phosphalkyne • phosphalkene • heterocycles • phosphalkenylborane

- [1] (a) M. V. R. Reddy, H. C. Brown, P. V. Ramachandran, *ACS Symp. Ser.* **2001**, *783*, 220–234.; (b) P. V. Ramachandran, H. C. Brown, *ACS Symp. Ser.* **2001**, *783*, 1–15.; (c) H. C. Brown, P. V. Ramachandran, *Spec. Publ. - R. Soc. Chem.* **1997**, *201*, 151–162.; (d) C. C. Chong, R. Kinjo, *ACS Catalysis* **2015**, 3238–3259.
- [2] (a) C. M. Vogels, S. A. Westcott, *Curr. Org. Chem.* **2005**, *9*, 687–699.; (b) G. C. Fu, *Transition Met. Org. Synth. (2nd Ed.)* **2004**, *2*, 193–198.; (c) G. C. Fu, *Transition Met. Org. Synth.* **1998**, *2*, 141–146.; (d) G. C. Fu, D. A. Evans, A. R. Muci, *Adv. Catal. Processes* **1995**, *1*, 95–121.; (e) S. A. Westcott, P. Nguyen, H. P. Blom, N. J. Taylor, T. B. Marder, R. T. Baker, J. C. Calabrese, *Spec. Publ. - R. Soc. Chem.* **1994**, *143*, 68–71.
- [3] H. C. Brown, *Tetrahedron* **1961**, *12*, 117.
- [4] (a) I. A. Cade, M. J. Ingleson, *Chem.-Eur. J.* **2014**, *20*, 12874–12880.; (b) C. Eller, G. Kehr, C. G. Daniliuc, R. Frohlich, G. Erker, *Organometallics* **2013**, *32*, 384–386.; (c) G. Kehr, G. Erker, *Chem. Commun.* **2012**, *48*, 1839–1850.
- [5] J. R. Lawson, E. R. Clark, I. A. Cade, S. A. Solomon, M. J. Ingleson, *Angew. Chem. Int. Ed.* **2013**, *52*, 7518–7522. *Angew. Chem.* **2013**, *125*, 7666–7670.
- [6] J. S. McGough, S. M. Butler, I. A. Cade, M. J. Ingleson, *Chem. Sci.* **2016**, *7*, 3384–3389.
- [7] (a) A. Rodriguez, R. A. Olsen, N. Ghaderi, D. Scheschkewitz, T. S. Tham, L. J. Mueller, G. Bertrand, *Angew. Chem. Int. Ed.* **2004**, *43*, 4880–4883. *Angew. Chem.* **2004**, *116*, 4988–4991.; (b) D. Scheschkewitz, H. Amii, H. Gornitzka, W. W. Schoeller, D. Bourissou, G. Bertrand, *Science* **2002**, *295*, 1880–1881.; (c) A. Rodriguez, F. S. Tham, W. W. Schoeller, G. Bertrand, *Angew. Chem. Int. Ed.* **2004**, *43*, 4876–4880. *Angew. Chem.* **2004**, *116*, 4984–4988.; (d) G. Fuks, N. Saffon, L. Maron, G. Bertrand, D. Bourissou, *J. Am. Chem. Soc.* **2009**, *131*, 13681.
- [8] (a) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, *54*, 6400–6441. *Angew. Chem.* **2015**, *127*, 6498–6541.; (b) D. W. Stephan, *J. Am. Chem. Soc.* **2015**, *137*, 10018–10032.; (c) D. W. Stephan, *Accs Chem. Res.* **2015**, *48*, 306–316.; (d) D. W. Stephan, G. Erker, *Chem. Sci.* **2014**, *5*, 2625–2641.
- [9] (a) G. Becker, *Z. Anorg. Allg. Chem.* **1976**, *423*, 242–254.; (b) M. J. Hopkinson, H. W. Kroto, J. F. Nixon, N. P. C. Simmons, *J. Chem. Soc. Chem. Commun.* **1976**, 513–514.; (c) M. C. Simpson, J. D. Protasiewicz, *Pure Appl. Chem.* **2013**, *85*, 801–815.; (d) J. Dugai-Tessier, E. D. Conrad, G. R. Dake, D. P. Gates, *Phosphorus(III) Ligands in Homogeneous Catalysis* **2012**, 321–341.; (e) J. I. Bates, J. Dugal-Tessier, D. P. Gates, *Dalton Trans.* **2010**, *39*, 3151–3159.; (f) K. Naka, *Organomet. News* **2008**, 39.
- [10] (a) G. Becker, M. Rossler, W. Uhl, *Z. Anorg. Allg. Chem.* **1981**, *473*, 7–19.; (b) R. Appel, A. Westerhaus, *Tetrahedron Lett.* **1981**, *22*, 2159–2160.
- [11] (a) R. L. Falconer, C. A. Russell, *Coord. Chem. Rev.* **2015**, *297*, 146–167.; (b) P. Le Floch, *Coord. Chem. Rev.* **2006**, *250*, 627–681.; (c) C. C. Cummins, *Angew. Chem. Int. Ed.* **2006**, *45*, 862–870. *Angew. Chem.* **2006**, *118*, 876–884.; (d) M. Regitz, P. Binger, *Angew. Chem. Int. Ed.* **1988**, *27*, 1484–1508. *Angew. Chem.* **1988**, *100*, 1541–1565.
- [12] G. Becker, W. Becker, R. Knebl, H. Schmidt, U. Hildenbrand, M. Westerhausen, *Phos. Sulf. Silicon Relat. Elem.* **1987**, *30*, 349–352.
- [13] F. Meyer, P. Paetzold, U. Englert, *Chem. Ber.* **1994**, *127*, 93–95.
- [14] (a) R. W. Miller, J. T. Spencer, *Organometallics* **1996**, *15*, 4293–4300.; (b) P. N. Condict, M. A. Fox, R. Greatrex, C. Jones, D. L. Ormsby, *Chem. Commun.* **2002**, 1448–1449.
- [15] J. H. Barnard, S. Yruegas, S. A. Couchman, D. J. D. Wilson, J. L. Dutton, C. D. Martin, *Organometallics* **2016**, *35*, 929–931.
- [16] P. Binger, F. Sandmeyer, C. Kruger, J. Kuhnigk, R. Goddard, G. Erker, *Angew. Chem. Int. Ed.* **1994**, *33*, 197–198. *Angew. Chem.* **1994**, *106*, 213–215.
- [17] A. S. Ionkin, S. N. Ignateva, B. A. Arbutov, *Russ. Chem. Bull.* **1990**, *6*, 1315–1315.
- [18] S. L. Choong, W. D. Woodul, C. Schenk, A. Stasch, A. F. Richards, C. Jones, *Organometallics* **2011**, *30*, 5543–5550.
- [19] M. Schmitz, R. Goller, U. Bergstrasser, S. Leininger, M. Regitz, *Eur. J. Inorg. Chem.* **1998**, 227–235.
- [20] D. J. Parks, R. E. v. H. Spence, W. E. Piers, *Angew. Chem. Int. Ed.* **1995**, *34*, 809–811. *Angew. Chem.* **1995**, *107*, 895–897.
- [21] (a) P. M. Esteves, K. K. Laali, *Organometallics* **2004**, *23*, 3701–3713.; (b) J. C. T. R. C.-S. Laurent, M. A. King, H. W. Kroto, J. F. Nixon, R. J. Suffolk, *J. Chem. Soc. Dalton Trans.* **1983**, 755–759.
- [22] (a) M. A. Dureen, C. C. Brown, D. W. Stephan, *Organometallics* **2010**, *29*, 6594–6607.; (b) M. A. Dureen, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 8396–8398.
- [23] (a) G. He, O. Shynkaruk, M. W. Lui, E. Rivard, *Chem. Rev.* **2014**, *114*, 7815–7880.; (b) R. T. Paine, H. Noth, *Chem. Rev.* **1995**, *95*, 343.
- [24] S. J. Geier, T. M. Gilbert, D. W. Stephan, *Inorg. Chem.* **2011**, *50*, 336–344.
- [25] R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, Ed.: John Wiley & Sons, Inc., Hoboken, New Jersey, **2009**.
- [26] H. J. Reich, R. R. Dykstra, *Organometallics* **1994**, *13*, 4578–4585.
- [27] (a) R. B. Bedford, D. E. Hibbs, A. F. Hill, M. B. Hursthouse, M. A. Malik, C. Jones, *Chem. Commun.* **1996**, 1895–1896.; (b) R. B. Bedford, A. F. Hill, C. Jones, A. J. P. White, D. J. Williams, J. D. E. T. Wilton-Ely, *Organometallics* **1998**, *17*, 4744–4753.
- [28] V. K. Greenacre, N. Trathen, I. R. Crossley, *Organometallics* **2015**, *34*, 2533–2542.
- [29] S. J. Geier, T. M. Gilbert, D. W. Stephan, *J. Am. Chem. Soc.* **2008**, *130*, 12632–12633.
- [30] For examples of crystalline phosphalkenes, see: (a) S. T. Liddle, K. Izod, *Organometallics* **2004**, *23*, 5550–5559.; (b) N. Yamada, K. Abe, K. Toyota, M. Yoshifuji, *Org. Lett.* **2002**, *4*, 569–572.; (c) S. Ito, S. Sekiguchi, M. Yoshi fuji, *Eur. J. Org. Chem.* **2003**, 4838–4841.; (d) S. Aldridge, C. Jones, P. C. Junk, A. F. Richards, M. Waugh, *J. Organomet. Chem.* **2003**, *665*, 127–134.

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