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## Phosphorus Heterocycles

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## Facile Phenylphosphinidene Transfer Reactions from Carbene–Phosphinidene Zinc Complexes

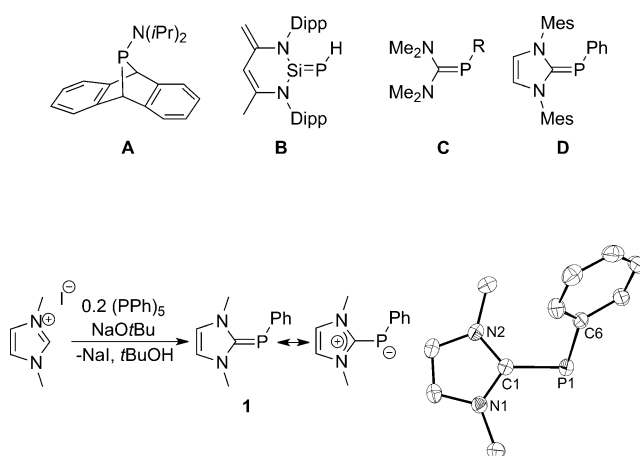
Tetiana Krachko, Mark Bispinghoff, Aaron M. Tondreau, Daniel Stein, Matthew Baker, Andreas W. Ehlers, J. Chris Slootweg,\* and Hansjörg Grützmacher\*

Dedicated to Professor Evamarie Hey-Hawkins on the occasion of her 60th birthday

**Abstract:** Phosphinidenes [R-P] are convenient  $P_1$  building blocks for the synthesis of a plethora of organophosphorus compounds. Thus far, transition-metal-complexed phosphinidenes have been used for their singlet ground-state reactivity to promote selective addition and insertion reactions. One disadvantage of this approach is that after transfer of the  $P_1$  moiety to the substrate, a challenging demetallation step is required to provide the free phosphine. We report a simple method that enables the Lewis acid promoted transfer of phenylphosphinidene, [PhP], from NHC=PPh adducts (NHC=N-heterocyclic carbene) to various substrates to produce directly uncoordinated phosphorus heterocycles that are difficult to obtain otherwise.

Considerable effort has been devoted to the development of phosphinidene [R-P] transfer agents<sup>[1,2]</sup> that do not require a metal.<sup>[3]</sup> Cummins and co-workers developed the unprotected dibenzo-7 $\lambda$ ,3-phosphanorbornadiene **A** as a source of the transient [iPr<sub>2</sub>NP], which undergoes a [1+4]-cycloaddition with 1,3-cyclohexadiene.<sup>[4]</sup> Driess and co-workers successfully transferred the parent phosphinidene [HP] from phosphasilene **B** (Dipp = 2,6-diisopropylphenyl) to an N-heterocyclic carbene,<sup>[5]</sup> and Weber et al. demonstrated the acyclic carbene–phosphinidene adducts **C** (R = *t*Bu, Cy, 1-Ad, Ph, Mes) to be viable [RP] transfer agents to diphenylketene.<sup>[6]</sup> Interestingly, Arduengo and co-workers showed that the Lewis acid BPh<sub>3</sub> induces formation of cyclopolyphosphines (PPh)<sub>*n*</sub> (*n* = 3–5) from <sup>Mes</sup>NHC=PPh **D**,<sup>[7]</sup> but no transfer reactions of the extruded phenylphosphinidene

moiety have been reported to date. This inspired us to target the sterically little encumbered <sup>Me</sup>NHC=PPh (**1**; Scheme 1) and study its ability to transfer [PhP] to suitable substrates in the presence of an appropriate Lewis acid.



**Scheme 1.** Synthesis of <sup>Me</sup>NHC=PPh (**1**; left) and molecular structure (right; hydrogen atoms and C<sub>6</sub>H<sub>6</sub> solvent molecule are omitted for clarity, one crystallographic independent molecule is shown). Selected bond lengths [Å] and angles [°] (values for the second molecule in square brackets): P1–C1 1.7917(14) [1.7911(15)], P1–C6 1.8157(16) [1.8132(14)], N1–C1 1.359(2) [1.3546(19)], N2–C1 1.3562(18) [1.356(2)], C1–P1–C6 101.30(6) [99.98(7)], N1–C1–N2 104.82(11) [105.15(13)], N2–C1–P1–C6 48.01(16) [50.42(15)].

First, we developed a scalable, efficient one-pot synthesis of carbene–phosphinidene adduct <sup>Me</sup>NHC=PPh (**1**) that avoids the need for free carbenes. Reaction of 1,3-dimethylimidazolium iodide with (PPh)<sub>5</sub> and sodium *tert*-butoxide in THF afforded **1** after a simple work-up (removal of all volatiles under reduced pressure, extraction into toluene, and crystallization) as an orange solid in 95% yield. The molecular structure of **1** ( $\delta^{31}\text{P}$  (C<sub>6</sub>D<sub>6</sub>) = –49.1 ppm; Scheme 1, right),<sup>[8]</sup> when compared to the bulkier <sup>Me</sup>NHC=PPh reported by Hey-Hawkins et al. ( $\delta^{31}\text{P}$  (C<sub>6</sub>D<sub>6</sub>) = –73.8 ppm),<sup>[9]</sup> displays a slightly elongated P1–C1 bond [1.7917(14)/1.7911(15) vs. 1.768(4) Å], a more acute C1–P1–C6 angle [101.30(6)/99.98(7) vs. 104.6(2)°], and a larger dihedral angle between the imidazole plane and the P1–C6 bond [48.01(16)/50.42(15) vs. 32.5(4)°], thus indicating considerable ylide character.<sup>[9]</sup> Beside the nature of the carbene moiety,<sup>[10]</sup> the P substituent also has a marked influence on the

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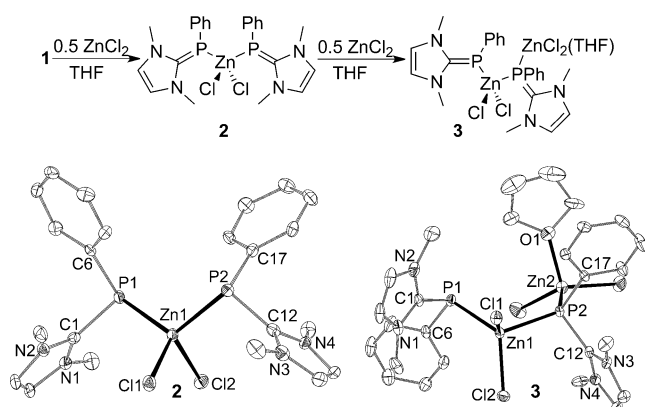
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structure<sup>[11]</sup> and thus the  $\delta^{31}\text{P}$  chemical shift of the carbene–phosphinidene adduct.  $^{\text{Mes}}\text{NHC}=\text{PPh}$  **D**<sup>[12]</sup> (93%) and  $^{\text{Dipp}}\text{NHC}=\text{PPh}$ <sup>[10]</sup> (87%) were also conveniently prepared by this method, thus complementing the known procedures for making carbene–phosphinidene adducts.<sup>[13]</sup>

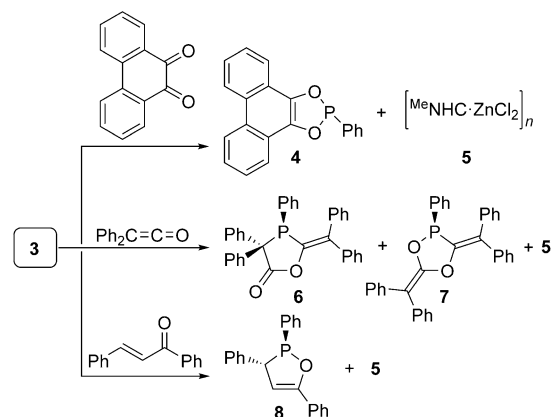
Next, we targeted the synthesis of a Lewis acid adduct of **1** that can controllably release phenylphosphinidene and, ideally, simultaneously capture the free carbene. Treatment of **1** with  $\text{BPh}_3$ ,  $\text{AlCl}_3$ ,  $\text{MgCl}_2$ , or  $\text{Zn}(\text{OAc})_2$  merely resulted in the direct formation of cyclopolyphosphines, which is consistent with Arduengo's observations.<sup>[7,14]</sup> However, slow addition of 0.5 equiv of  $\text{ZnCl}_2$  to a THF solution of **1** afforded zinc adduct **2** ( $\text{I}_2\cdot\text{ZnCl}_2$ ) as a pale yellow precipitate (76%; Scheme 2, top), which is poorly soluble in common organic



solvents. Single crystals suitable for X-ray diffraction analysis were obtained from DME, which unequivocally established the formation of a 2:1 complex of a carbene–phosphinidene adduct (Scheme 2, bottom).<sup>[8,15]</sup> Upon complexation, significant structural changes occur: the central P–C bonds [1.818(4), 1.827(4) Å] become longer, the C–P–C angles more acute [100.2(2), 100.8(2)°], and the dihedral angles smaller [31.1(4), 42.9(4)°; Scheme 2, bottom].<sup>[8]</sup> Reaction of **1** with 1 equiv of  $\text{ZnCl}_2$  in THF afforded the soluble 1:1 adduct **3**, which was isolated as colorless crystals in 87% yield (Scheme 2, top). The structure of **3** in the solid state shows a di-zinc complex that can be related to the one of **2** by adding  $\text{ZnCl}_2(\text{THF})$  to P2 such that one  $^{\text{Me}}\text{NHC}=\text{PPh}$  ligand bridges two Zn centers via P2, while the other  $^{\text{Me}}\text{NHC}=\text{PPh}$  unit takes a terminal position (Scheme 2, bottom).<sup>[8]</sup> Consequently, the phosphorus atoms are inequivalent, yet in solution, even at  $-80^\circ\text{C}$ , only one  $\delta^{31}\text{P}$  resonance was observed in  $[\text{D}_8]\text{THF}$  at  $-88.1$  ppm, thus indicating that **3** has a different structure in solution

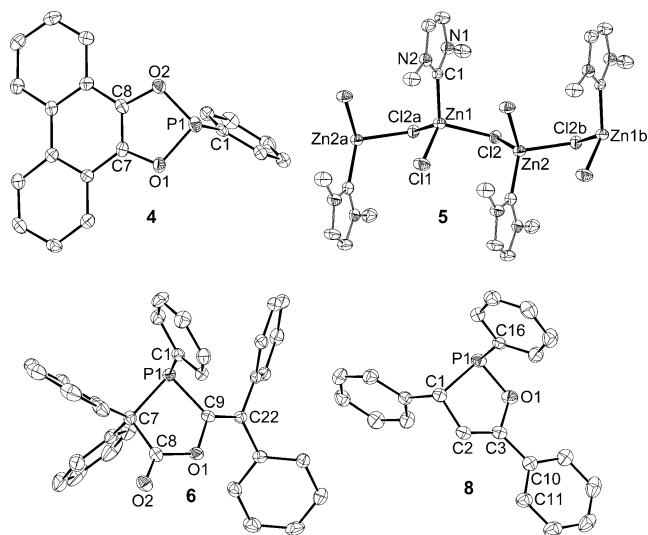
(either monomeric or a dimer with symmetric cyclic  $\text{Zn}_2\text{P}_2$  core).

The soluble Lewis adduct **3** was tested as a phosphinidene-transfer agent with phenanthrene-9,10-quinone, diphenylketene, and *trans*-chalcone as suitable acceptors (Scheme 3).<sup>[16]</sup>



**Scheme 3.** Reactivity of **3** towards phenanthrene-9,10-quinone, diphenylketene, and *trans*-chalcone.

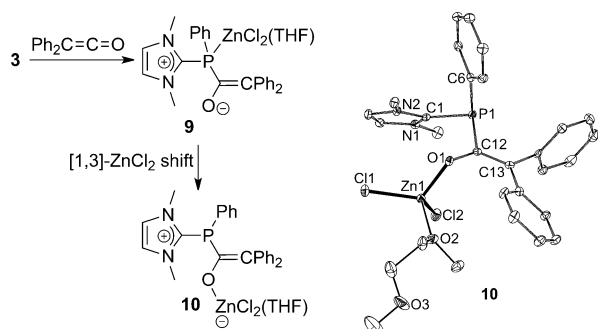
Treatment of **3** with phenanthrene-9,10-quinone in THF afforded phosphonite **4** as a pale green solid (46%;  $\delta^{31}\text{P}$  ( $\text{C}_6\text{D}_6$ ) = 183.3 ppm), which was characterized by single-crystal X-ray diffraction analysis (Figure 1).<sup>[8]</sup> Previously, **4** has only been accessible through thermal fragmentation of the corresponding phosphorane.<sup>[17]</sup> Heterocycle **4** was devoid of zinc chloride, which was transferred to the carbene to



**Figure 1.** Molecular structures of **4**, **5** (only a fragment is shown), **6**, and **8**. Selected bond lengths [Å] and angles [°] for **4**: P1–O1 1.6859(19), P1–O2 1.675(2), P1–C1 1.827(3), C7–C8 1.347(4). **5**: Zn1–Cl1 2.2179(18), Zn1–Cl2 2.3670(11), Zn1–Cl2a 2.3670(11), Zn2a–Cl2a 2.3597(12), Zn1–C1 2.021(6), N1–C1 1.329(8), N2–C1 1.377(8); **6**: P1–C1 1.826(2), P1–C7 1.902(2), P1–C9 1.824(2), O1–C8 1.365(2), O1–C9 1.415(2), O2–C8 1.197(2), C7–C8 1.526(3), C9–C22 1.340(3); **8**: P1–O1 1.6636(13), P1–C1 1.876(2), P1–C16 1.8241(18), O1–C3 1.400(2), C1–C2 1.503(3), C2–C3 1.325(3); C2–C3–C10–C11  $-3.2(3)$ .

afford NHC complex **5** as an insoluble, colorless, crystalline solid.<sup>[18]</sup> The molecular structure of **5** displays a one-dimensional coordination polymer with unusual zigzag zinc chloride chains with almost identical Zn–Cl distances [Zn1–Cl2 2.3670(11), Zn2–Cl2 2.3597(12) Å] and the NHC moiety positioned orthogonally to the main chain [Zn1–C1 2.021(6) Å; Figure 1].<sup>[8,19]</sup>

Reaction of di-zinc complex **3** with 4 equiv of diphenylketene afforded phosphorus heterocycles **6** and **7** in a 2:3 ratio ( $\delta^{31}\text{P}$  ([D<sub>8</sub>]THF): –2.9 and 90.9 ppm, respectively; Scheme 3) together with NHC complex **5**. Whereas 1,4,2-dioxaphospholane **7** was reported previously,<sup>[6]</sup> 1,3-oxaphospholan-5-one **6** is new, and only derivatives thereof lacking the exocyclic C=C double bond are known.<sup>[20,21]</sup> The molecular structure of **6** was unambiguously established by single-crystal X-ray analysis (Figure 1).<sup>[8,16]</sup> It shows a five-membered heterocycle resulting from a formal [1+2+2] cycloaddition, where the endocyclic P1–C9 [1.824(2) Å] and exocyclic P1–C1 bonds [1.826(2) Å] are of similar length, while the endocyclic P1–C7 bond [1.902(2) Å] is significantly elongated, most likely due to steric hindrance from neighboring phenyl rings. Treatment of **3** with only 2 equiv of diphenylketene yielded **10** after work-up as an off-white solid (82%,  $\delta^{31}\text{P}$  ([D<sub>8</sub>]THF) = –16.6 ppm; Scheme 4), which contained traces of **6** and **7**. Single crystals



**Scheme 4.** Synthesis of intermediate **10** (left) and molecular structure of **10** (right; hydrogen atoms, one disordered DME molecule, and toluene solvent are omitted for clarity). Selected bond lengths [Å] and angles [°] for **10**: P1–C1 1.835(3), P1–C6 1.838(4), P1–C12 1.854(3), O1–C12 1.330(4), C12–C13 1.362(4); O1–C12–C13 126.3(3).

suitable for X-ray diffraction analysis were obtained from DME, which established the formation of a 1:1 adduct (Scheme 4, right).<sup>[8]</sup> The structural parameters are consistent with the formula shown in Scheme 4 [P1–C1 1.835(3) Å, P–C12 1.854(3) Å, C12–O1 1.330(4) Å are single bonds, C12–C13 1.362(4) Å is a double bond]. Calculations at  $\omega\text{B97X-D}/6\text{-31G(d,p)}$ <sup>[14]</sup> reveal that nucleophilic attack of the phosphorus atom of **3** at the ketene carbonyl carbon first gives adduct **9** ( $\Delta G = 11.0 \text{ kcal mol}^{-1}$ ;  $\Delta G_a = 13.1 \text{ kcal mol}^{-1}$ ; Scheme 4, top left), which affords **10** after ZnCl<sub>2</sub> transfer from P to O ( $\Delta G = -18.3 \text{ kcal mol}^{-1}$ ;  $\Delta G_a = 13.1 \text{ kcal mol}^{-1}$ ). Furthermore, we confirmed experimentally that intermediate **10** is able to react with either the C=C or C=O double bond of another equiv of diphenylketene to form **6** and **7** after extrusion of Zn complex **5**.

Treatment of **3** with 2 equiv of *trans*-chalcone afforded the rare tricoordinate oxo-3-phospholene **8** as a single diastereomer in 80% yield ( $\delta^{31}\text{P}$  (C<sub>6</sub>D<sub>6</sub>) = 133.9 ppm; Scheme 3), simply after filtering off [M<sup>c</sup>NHC·ZnCl<sub>2</sub>]<sub>n</sub> **5** (83%), extraction into toluene, and crystallization. Such an unprotected five-membered heterocycle has only been prepared once before, through a two-step procedure using an electrophilic phosphinidene complex followed by demetallation.<sup>[22]</sup> The molecular structure of **8** firmly establishes the phenyl rings to be in the *trans* position and shows that the third phenyl ring (on C3) is in conjugation with the C1=C2 double bond in the ring [C2–C3–C10–C11 –3.2(3)°; Figure 1].<sup>[8]</sup> We turned to DFT calculations to provide insight into the formation of **8**.<sup>[14]</sup> In contrast to the ketene, where the carbonyl carbon is attacked first, now the reactions start with coordination of *trans*-chalcone to **3** by Zn–O bond formation, which selectively affords **8** after P–C bond formation and subsequent ring closure by P–O bond formation and elimination of (NHC)Zn complex **5** (see the Supporting Information).

In summary, the sterically little hindered carbene–phosphinidene adduct M<sup>c</sup>NHC=PPh allows the synthesis of new zinc complexes, of which the soluble Lewis adduct **3** selectively transfers a phenylphosphinidene fragment, thereby providing access to uncoordinated phosphorus heterocycles. The driving force for these reactions is likely the formation of the insoluble coordination polymer [M<sup>c</sup>NHC·ZnCl<sub>2</sub>]<sub>n</sub> **5**, which explains why only ZnCl<sub>2</sub> proved to be efficient to date. Highly reactive or unstable main-group fragments can be stabilized by NHCs,<sup>[23]</sup> however, their transfer to other substrates has very rarely been observed.<sup>[24]</sup> The Lewis acid promoted transfer reaction may help to develop this chemistry further.

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## Conflict of interest

The authors declare no conflict of interest.

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