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- Title: Facile Phenylphosphinidene Transfer Reactions from Carbene-Phosphinidene Zinc Complexes
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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201703672 Angew. Chem. 10.1002/ange.201703672

Link to VoR: http://dx.doi.org/10.1002/anie.201703672 http://dx.doi.org/10.1002/ange.201703672

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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  $\rm 60^{th}\ Birthday$ 

**Abstract:** Phosphinidenes [R-P] are convenient P1 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, promoting selective addition and insertion reactions. One disadvantage of this approach is that after transfer of the P<sub>1</sub> moiety to the substrate a challenging demetallation step is required to provide the free phosphine. Here we report a simple method which allows 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 efforts have been devoted to the development of phosphinidene transfer agents<sup>1,2</sup> which 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 [iPr2NP] that 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 a Nheterocyclic carbene,<sup>5</sup> and Weber et al. demonstrated the acyclic carbene-phosphinidene adducts C (R = tBu, 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 BPh3 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 MeNHC=PPh (1; Scheme 1) and study its ability to transfer [PhP] to suitable substrates in the presence of an appropriate Lewis acid.





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using free carbenes. Reaction of 1,3-dimethylimidazolium iodide with (PPh)5 and sodium tert-butoxide in THF afforded 1 after a simple workup (removal of all volatiles in vacuo, extraction into toluene and crystallization) as an orange solid in 95% yield. The molecular structure of 1 ( $\delta^{31}$ 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=PMes reported by Hey-Hawkins *et al.* ( $\delta^{31}$ 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)°], indicating considerable ylide character.<sup>9</sup> Beside the nature of the carbene moiety,10 also the P-substituent has a marked influence on the structure  $^{11}$  and thus the  $\delta^{31}{\rm P}$  chemical shift of the carbenephosphinidene adduct. MesNHC=PPh D<sup>12</sup> (93%) and DippNHC=PPh<sup>10</sup> (87%) were also conveniently prepared by this method, complementing the known procedures for making carbene-phosphinidene adducts.<sup>13</sup>



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)].

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 BPh<sub>3</sub>, AlCl<sub>3</sub>, MgCl<sub>2</sub> or resulted in the direct formation  $Zn(OAc)_2$ merely of cyclopolyphosphines, consistent with Arduengo's observations.<sup>7,14</sup> But, slow addition of 0.5 equiv of ZnCl2 to a THF solution of 1 afforded zinc adduct 2 (12·ZnCl2) 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).8, 15 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),  $100.8(2)^{\circ}$  and the dihedral angles smaller [31.1(4), 42.9(4)^{\circ}] (Scheme 2, bottom).<sup>8</sup> Reaction of 1 with 1 equiv of ZnCl<sub>2</sub> 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 dizinc complex that can be related to the one of 2 by adding ZnCl<sub>2</sub>(THF) to P2 such that one MeNHC=PPh ligand bridges via P2 two Zn centers, while the other MeNHC=PPh unit takes a terminal position (Scheme 2, bottom).8 Consequently, the phosphorus atoms are inequivalent, yet in

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solution, even at -80 °C, only one  $\delta^{31}$ P resonance was observed in THF*d*<sub>8</sub> at -88.1 ppm indicating that in solution **3** has a different structure (either monomeric or a dimer with symmetric cyclic Zn<sub>2</sub>P<sub>2</sub> core).



Scheme 2. Synthesis of ZnCl<sub>2</sub> complexes 2 and 3 (top) and molecular structures (bottom) of 2 (DME solvent molecule omitted) and 3 (THF solvent molecule omitted). Selected bond lengths [Å] and angles [°] for 2: Zn1–P1 2.3959(11), Zn1–P2 2.3867(11), P1–C1 1.818(4), P1–C6 1.826(4), P2–C12 1.827(4), P2–C17 1.841(5); C1–P1–C6 100.2(2), C12–P2–C17 100.8(2); N2–C1–P1–C6 31.1(4), N4–C12–P2–C17 42.9(4). 3: Zn1–P1 2.3793(14), Zn1–P2 2.4386(13), Zn2–P2 2.4110(14), P1–C1 1.819(4), P1–C6 1.832(4), P2–C12 1.818(4), P2–C17 1.833(4); N2–C1–P1–C6 33.3(4).

The soluble Lewis adduct **3** was tested as phosphinidene transfer agent with phenanthrene-9,10-quinone, diphenylketene and *trans*chalcone as suitable acceptors (Scheme 3).<sup>16</sup> Treatment of **3** with phenanthrene-9,10-quinone in THF afforded phosphonite **4** as a pale green solid (46%;  $\delta^{31}P$  (C<sub>6</sub>D<sub>6</sub>) = 183.3 ppm), which was characterized by single-crystal X-ray diffraction analysis (Figure 1).<sup>8</sup> Previously, **4** has only been accessible via thermal fragmentation of the corresponding phosphorane.<sup>17</sup> Heterocycle **4** was devoid of zinc chloride, which was transferred to the carbene affording NHC complex **5** as an insoluble, colorless, crystalline solid.<sup>18</sup> The molecular structure of **5** displays a onedimensional coordination polymer with unusual zigzag Zn–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–Cl 2.021(6) Å] (Figure 1).<sup>8,19</sup>



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

Reaction of di-zinc complex 3 with 4 equiv of diphenylketene afforded phosphorus heterocycles **6** and **7** in a 2:3 ratio ( $\delta^{31}$ P (THF- $d_8$ ): -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> 1,3oxaphospholan-5-one 6 is new and only derivatives thereof lacking the exocyclic C=C double bond are known.20,21 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 bond [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 sterical hindrance of neighboring phenyl rings. Treatment of 3 with only 2 equiv. of diphenylketene yielded after work-up 10 as an off-white solid (82%,  $\delta^{31}$ P (THF- $d_8$ ) = -16.6 ppm; Scheme 4), which contained traces of 6 and 7. Single crystals suitable for X-ray diffraction analysis were obtained from DME, which established the formation of a 1:1 adduct (Scheme 4, right).8 The structural parameters are in accord with the formula shown in Scheme 4 [P1-C1 1.835(3) Å, P1-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  $\omega$ B97X-D/6-31G(d,p)<sup>14</sup> reveal that nucleophilic attack of the phosphorus atom of 3 at the ketene's carbonyl carbon first gives adduct 9 ( $\Delta G = 11.0 \text{ kcal} \cdot \text{mol}^{-1}$ ;  $\Delta G_a = 13.1 \text{ kcal} \cdot \text{mol}^{-1}$ <sup>1</sup>; Scheme 4, top left), which affords **10** after ZnCl<sub>2</sub> transfer from P to O  $(\Delta G = -18.3 \text{ kcal} \cdot \text{mol}^{-1}; \Delta G_a = 13.1 \text{ kcal} \cdot \text{mol}^{-1})$ . 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 forming 6 and 7, after extrusion of Zn complex 5.

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**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), Zn2–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).



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

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1.838(4), P1-C12 1.854(3), O1-C12 1.330(4), C12-C13 1.362(4); O1-C12-C13 126.3(3).

Treatment of 3 with 2 equiv. of trans-chalcone afforded the rare tricoordinate oxo-3-phospholene 8 as a single diastereomer in 80% yield  $(\delta^{31}P (C_6D_6) = 133.9 \text{ ppm};$  Scheme 3), simply after filtering off  $[^{Me}NHC \cdot ZnCl_2]_n$  5 (83%), extraction into toluene and crystallization. Such an unprotected, five-membered heterocycle has only been prepared once before, via a two-step procedure using an electrophilic phosphinidene complex followed by demetallation.<sup>22</sup> The molecular structure of 8 firmly established the phenyl rings to be in 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).8 We resorted again DFT calculations to provide insight into the formation of  $8.^{14}$  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 <sup>Me</sup>NHC=PPh allows the synthesis of new zinc complexes, of which the soluble Lewis adduct **3** selectively transfers a phenylphosphinidene fragment providing access to uncoordinated phosphorus heterocycles. The driving force for these reactions is likely the formation of the insoluble coordination polymer [<sup>Me</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 been very rarely observed.<sup>24</sup> The Lewis acid promoted transfer reaction may help to develop this chemistry further.

#### Acknowledgements

This work was supported by the European Union (Marie Curie ITN SusPhos, Grant Agreement No. 317404). Prof. Dr. David Scheschkewitz is gratefully acknowledged for fruitful discussions.

**Keywords:** adducts • N-heterocyclic carbenes • phosphinidenes • Lewis acids • phosphorus heterocycle

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**Phosphinidene transfer**: ZnCl<sub>2</sub> promoted phosphinidene transfer reactions of the sterically unencumbered carbene-phosphinidene adduct <sup>Me</sup>NHC=PPh to various substrates (**S**) are demonstrated. These unprecedented reactions provided access to new uncomplexed phosphorus heterocycles, which are difficult to obtain otherwise.

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