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Phosphorus Heterocycles

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Facile Phenylphosphinidene Transfer Reactions from Carbene–Phosphinidene Zinc Complexes

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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^[1,2] that do not require a metal.^[3] Cummins and co-workers developed the unprotected dibenzo-7 λ^3 -phosphanorbornadiene **A** as a source of the transient [iPr₂NP], which undergoes a [1+4]-cycloaddition with 1,3-cyclohexadiene.^[4] Driess and co-workers successfully transferred the parent phosphinidene [HP] from phosphasilene **B** (Dipp = 2,6-diisopropylphenyl) to an N-heterocyclic carbene,^[5] 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.^[6] Interestingly, Arduengo and co-workers showed that the Lewis acid BPh₃ induces formation of cyclopolyphosphines (PPh)_{*n*} (*n* = 3–5) from ^{Mes}NHC=PPh **D**,^[7] but no transfer reactions of the extruded phenylphosphinidene

moiety have been reported to date. This inspired us to target the sterically little encumbered ^{Mes}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 ^{Mes}NHC=PPh (**1**; left) and molecular structure (right; hydrogen atoms and C₆H₆ 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 ^{Mes}NHC=PPh (**1**) that avoids the need for free carbenes. Reaction of 1,3-dimethylimidazolium iodide with (PPh)₅ 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** ($\delta^{31}P$ (C₆D₆) = –49.1 ppm; Scheme 1, right),^[8] when compared to the bulkier ^{Mes}NHC=PMes reported by Hey-Hawkins et al. ($\delta^{31}P$ (C₆D₆) = –73.8 ppm),^[9] 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.^[9] Beside the nature of the carbene moiety,^[10] the P substituent also has a marked influence on the

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

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_3 , AlCl_3 , MgCl_2 , or $\text{Zn}(\text{OAc})_2$ merely resulted in the direct formation of cyclopolyphosphines, which is consistent with Arduengo's observations.^[7,14] However, slow addition of 0.5 equiv of ZnCl_2 to a THF solution of **1** afforded zinc adduct **2** ($\text{1}_2\cdot\text{ZnCl}_2$) as a pale yellow precipitate (76%; Scheme 2, top), which is poorly soluble in common organic

Scheme 2. Synthesis of ZnCl_2 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). DME = dimethoxyethane, THF = tetrahydrofuran.

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)°], and the dihedral angles smaller [31.1(4), 42.9(4)°; Scheme 2, bottom].^[8] Reaction of **1** with 1 equiv of 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 $\text{MeNHC}=\text{PPh}$ ligand bridges two Zn centers via P2, while the other $\text{MeNHC}=\text{PPh}$ unit takes a terminal position (Scheme 2, bottom).^[8] Consequently, the phosphorus atoms are inequivalent, yet in solution, even at -80°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 Zn_2P_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).^[16]

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%; $\delta^{31}\text{P}$ (C_6D_6) = 183.3 ppm), which was characterized by single-crystal X-ray diffraction analysis (Figure 1).^[8] Previously, **4** has only been accessible through thermal fragmentation of the corresponding phosphorane.^[17] 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.^[18] 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].^[8,19]

Reaction of di-zinc complex **3** with 4 equiv of diphenylketene afforded phosphorus heterocycles **6** and **7** in a 2:3 ratio ($\delta^{31}\text{P}$ ([D₈]THF): –2.9 and 90.9 ppm, respectively; Scheme 3) together with NHC complex **5**. Whereas 1,4,2-dioxaphospholane **7** was reported previously,^[6] 1,3-oxaphospholan-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).^[8,16] 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 %, $\delta^{31}\text{P}$ ([D₈]THF) = –16.6 ppm; Scheme 4), which contained traces of **6** and **7**. Single crystals

Treatment of **3** with 2 equiv of *trans*-chalcone afforded the rare tricoordinate oxo-3-phospholene **8** as a single diastereomer in 80 % yield ($\delta^{31}\text{P}$ (C₆D₆) = 133.9 ppm; Scheme 3), simply after filtering off [^MNHC·ZnCl₂]_n **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.^[22] 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].^[8] We turned to 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 ^MNHC=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 [^MNHC·ZnCl₂]_n **5**, which explains why only ZnCl₂ proved to be efficient to date. Highly reactive or unstable main-group fragments can be stabilized by NHCs,^[23] however, their transfer to other substrates has very rarely been observed.^[24] The Lewis acid promoted transfer reaction may help to develop this chemistry further.

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).^[8] 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 $\omega\text{B97X-D/6-31G(d,p)}$ ^[14] 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 ZnCl₂ 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**.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: adducts · Lewis acids · N-heterocyclic carbenes · phosphinidenes · phosphorus heterocycles

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