Chapter 2

Facile Phenylphosphinidene Transfer Reactions from Carbene-Phosphinidene Zinc Complexes

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 to promote selective addition and insertion reactions. One disadvantage of this approach is that after transfer of the P₁ moiety to the substrate a challenging demetallation step is required to provide the free phosphine. In this chapter 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.

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2.1 Introduction

Considerable efforts have been devoted to the development of phosphinidene transfer agents\(^\text{[1,2]}\) which do not require a metal\(^\text{[3]}\). Cummins and co-workers developed the unprotected dibenzo-7,3-phosphanorbornadiene \(A\) as a source of the transient \([\text{iPr}_2\text{NP}],\) which undergoes a [1+4]-cycloaddition with 1,3-cyclohexadiene\(^\text{[4]}\). Driess and co-workers successfully transferred the parent phosphinidene \([\text{HP}]\) from phosphasilene \(B\) (Dipp = 2,6-diisopropylphenyl) to an N-heterocyclic carbene,\(^\text{[5]}\) and Weber et al. demonstrated the acyclic carbene-phosphinidene adducts \(C\) (R = tBu, Cy, 1-Ad, Ph, Mes) to be viable \([\text{RP}]\) transfer agents to diphenylketene.\(^\text{[6]}\) Interestingly, Arduengo and co-workers showed that the Lewis acid \(\text{BPh}_3\) induces formation of cyclopolyphosphines \((\text{PPh})_n\) \((n = 3–5)\) from \(\text{MesNHC}=\text{PPh} \ D,\)\(^\text{[7]}\) but no transfer reactions of the extruded phenylphosphinidene moiety have been reported to date. This inspired us to target the sterically little encumbered \(\text{MesNHC}=\text{PPh} \ (1; \text{Scheme 1})\) and study its ability to transfer \([\text{PhP}]\) to suitable substrates in the presence of an appropriate Lewis acid.

![Diagram](image)

2.2 Results and Discussion

First, we developed a scalable, efficient one-pot synthesis of carbene-phosphinidene adduct \(\text{MesNHC}=\text{PPh} \ (1)\) that avoids the need for free carbenes. Reaction of 1,3-dimethylimidazolium iodide with \((\text{PPh})_5\) 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 \(1\) \((\delta^{31}\text{P} \ (\text{C}_6\text{D}_6) = −49.1 \text{ ppm}; \text{Scheme 1, right}),\)^{[8]}
when compared to the bulkier MeNHC=PMes reported by Hey-Hawkins et al. ($\delta^{31}P$ (C$_6$D$_6$) = $\text{-73.8 ppm}$), 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)$^\circ$], and a larger dihedral angle between the imidazole plane and the P1–C6 bond [48.01(16)/50.42(15) vs. 32.5(4)$^\circ$], thus indicating considerable ylide character.$^9$ Beside the nature of the carbene moiety,$^{10}$ the P-substituent also has a marked influence on the structure$^{11}$ and thus the $\delta^{31}P$ chemical shift of the carbene-phosphinidene adduct. MesNHC=PPh D$^{[12]}$ (93%) and DippNHC=PPh$^{[10]}$ (87%) were also conveniently prepared by this method, thus complementing the known procedures for making carbene-phosphinidene adducts.$^{[13]}$

Scheme 1. Synthesis of MeNHC=PPh (1; left) and molecular structure (right; hydrogen atoms and C$_6$H$_6$ 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$_3$, AlCl$_3$, MgCl$_2$ or Zn(OAc)$_2$ merely resulted in the direct formation of cyclopolyphosphines, which is consistent with Arduengo’s observations.$^{[7,14]}$ But, slow addition of 0.5 equiv of ZnCl$_2$ to a THF solution of 1 afforded zinc adduct 2 (1$_2$·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).\cite{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].\cite{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 ZnCl$_2$(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).\cite{8} Consequently, the phosphorus atoms are inequivalent, yet in solution, even at −80 °C, only one $\delta^{31}$P resonance was observed in THF-$d_8$ at −88.1 ppm indicating that 3 has a different structure in solution (either monomeric or a dimer with symmetric cyclic Zn$_2$P$_2$ core).

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.
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).\(^{[16]}\) Treatment of 3 with phenanthrene-9,10-quinone in THF afforded phosphonite 4 as a pale green solid (46%; \(\delta^{31}P\) (C\(_6\)D\(_6\)) = 183.3 ppm), which was characterized by single-crystal X-ray diffraction analysis (Figure 1).\(^{[8]}\) Previously, 4 has only been accessible via thermal fragmentation of the corresponding phosphorane.\(^{[17]}\) Heterocycle 4 was devoid of zinc chloride, which was transferred to the carbene affording NHC complex 5 as an insoluble, colorless, crystalline solid.\(^{[18]}\) The molecular structure of 5 displays a one-dimensional 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–C1 2.021(6) Å] (Figure 1).\(^{[8,19]}\)

![Scheme 3. Reactivity of 3 towards phenanthrene-9,10-quinone, diphenylketene, and trans-chalcone.](image)

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,\textsuperscript{[6]} 1,3-oxaphosphan-5-one 6 is new and only derivatives thereof lacking the exocyclic C=C double bond are known.\textsuperscript{[20,21]}

![Molecular structures](image)

**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).

The molecular structure of 6 was unambiguously established by single crystal X-ray analysis (Figure 1).\textsuperscript{[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 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 steric hindrance of neighboring phenyl rings. Treatment of 3 with only 2 equiv. of diphenylketene yielded 10 after work-up as an off-white solid (82%, $\delta^{31}$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).\textsuperscript{[8]} The structural parameters are consistent with the
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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 ωB97X-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 (ΔG = 11.0 kcal·mol⁻¹; ΔG‡ = 13.1 kcal·mol⁻¹; Scheme 4, top left), which affords 10 after ZnCl₂ transfer from P to O (ΔG = -18.3 kcal·mol⁻¹; ΔG‡ = 13.1 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 forming 6 and 7 after extrusion of Zn complex 5.

![Scheme 4](image)

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).

Treatment of 3 with 2 equiv. of trans-chalcone afforded the rare tricoordinate oxo-3-phospholene 8 as a single diastereomer in 80% yield (δ³¹P (C₆D₆) = 133.9 ppm; Scheme 3), simply after filtering off [MeNHC·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 established the phenyl rings to be in trans position and shows
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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 Section 2.4).

2.3. Conclusion

In summary, the sterically little hindered carbene phosphinidene adduct \(^{Me}\)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 \([^{Me}\text{NHC}·\text{ZnCl}_2]\)_\(\text{n} 5\), which explains why only \(\text{ZnCl}_2\) 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.

2.4 Computational Section

Density functional calculations were performed with the Gaussian09 suite of software, revision D.01,[25] using the \(\omega\)B97X-D functional,[26] and the 6-31G(d,p) basis set.[27] All geometries have been computed and optimized in the gas phase. The stationary points were characterized by full vibration frequencies calculations as minima (no imaginary frequency) or transition states (one single imaginary frequency). When necessary, final proof for the position of the transition state was obtained by an IRC calculation. All coordinates are reported in angstroms, energies in kcal·mol\(^{-1}\).
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**Reaction of the phosphinidene zinc complex 3 with 1 equivalent of diphenylketene**

In principle, two different reaction pathways for the formation of 10 can be envisioned, i.e. the direct nucleophilic attack of the phosphorus atom at the ketene’s carbonyl carbon atom (A, Scheme 5) or the initial coordination of the ketene to 3 by Zn–O bond formation, followed by nucleophilic attack of the phosphorus atom (B, Scheme 6).

**A: Direct nucleophilic attack**

Calculations reveal that direct nucleophilic attack of the phosphorus atom of 3 at the ketene carbonyl carbon indeed is possible. After formation of adduct 9 ($\Delta G = 11.0 \text{ kcal} \cdot \text{mol}^{-1}$; $\Delta G^\ddagger = 13.1 \text{ kcal} \cdot \text{mol}^{-1}$), 10 is formed by ZnCl$_2$ transfer from P to O ($\Delta G = -18.3 \text{ kcal} \cdot \text{mol}^{-1}$; $\Delta G^\ddagger = 13.1 \text{ kcal} \cdot \text{mol}^{-1}$).

**Scheme 5. Relative energies for the pathway A (direct nucleophilic attack) leading from 3 and diphenylketene to 10.**

**B: Nucleophilic attack on a ZnCl$_2$ coordinated ketene**

Alternatively, replacing THF with the ketene in 3 by Zn–O bond formation could lead to formation of an intermediate II ($\Delta G = 10.6 \text{ kcal} \cdot \text{mol}^{-1}$). However, subsequent nucleophilic attack by the phosphorus atom at the carbonyl carbon has a significantly higher barrier ($\Delta G^\ddagger = 24.7 \text{ kcal} \cdot \text{mol}^{-1}$) than the direct attack (Pathway A).
Scheme 6. Relative energies for the pathway B leading from 3 and diphenylketene to 10.

**Reaction of the phosphinidene zinc complex 3 with trans-chalcone**

The reaction mechanism of the phosphinidene zinc complex 3 and *trans*-chalcone was envisioned to involve the P–Zn insertion intermediate VII akin to 10 (Scheme 8). To form VII, two possible reaction pathways have been evaluated, i.e. the direct nucleophilic attack by the phosphorus atom at the carbonyl carbon (A, Scheme 7) or initial coordination of *trans*-chalcone to 3 by Zn–O bond formation, followed by nucleophilic attack by the phosphorus atom (B, Scheme 8).

**A: Direct nucleophilic attack**

In contrast to the ketene, the direct nucleophilic attack on *trans*-chalcone is highly disfavored due to the repulsion between the carbonyl substituent and the coordinated THF. Therefore, P–C bond formation has an activation barrier of 28.8 kcal·mol\(^{-1}\) (\(\Delta G^\ddagger\); Scheme 7).

Scheme 7. Relative energies of products resulting from the addition of *trans*-chalcone to complex 3 (Pathway A).
B: Nucleophilic attack on a ZnCl₂ activated trans-chalcone

Coordination of trans-chalcone to 3 by Zn–O bond formation ($\Delta G = 0.9$ kcal·mol⁻¹; $\Delta G^\ddagger = 5.8$ kcal·mol⁻¹) activates trans-chalcone towards nucleophilic attack. This attack via a low energy transition state ($\Delta G^\ddagger = 16.0$ kcal·mol⁻¹) leads to the formation of a six-membered ring VI ($\Delta G = 11.1$ kcal·mol⁻¹), which after subsequent ring-opening in the presence of THF yields VII ($\Delta G = −0.3$ kcal·mol⁻¹; Scheme 8). Afterwards, nucleophilic attack of the oxygen atom at P takes place from the backside of the P–C carbene bond (at $\sigma^*$ MO of the P–C carbene bond), while simultaneously transferring ZnCl₂ to P, leads to the formation of intermediate VIII ($\Delta G = 5.2$ kcal·mol⁻¹; $\Delta G^\ddagger = 5.5$ kcal·mol⁻¹). The former intermediate VIII eliminating (NHC)Zn complex 5 yields product 8 ($\Delta G = −7.8$ kcal·mol⁻¹; $\Delta G^\ddagger = 16.2$ kcal·mol⁻¹; Scheme 9). The magnitude of all activation barriers in this pathway is fully consistent with mild experimental conditions of the reaction.

Scheme 8. Relative energies of products resulting from the addition of trans-chalcone to complex 3 (to the intermediate VII via pathway B).

Scheme 9. Relative energies of products resulting from the addition of trans-chalcone to complex 3 (to form 8 and 5).
2.5 Experimental Section

All syntheses were carried out under an atmosphere of dry argon employing standard Schlenk-line and glovebox techniques. Solvents were purified using an Innovative Technology PureSolv MD 7 solvent purification system. Deuterated solvents were purchased from Cambridge Isotope Laboratories. THF-$d_8$ and $C_6D_6$ were distilled from sodium benzophenone, whereas $CD_2Cl_2$ was dried over 4 Å molecular sieves before use. All reagents were used as received from commercial suppliers unless otherwise stated. The compounds 1,3-dimethylimidazolium iodide,$^{[28]}$ [DippNHCH-H][Cl]$^{[29]}$ diphenylketene$^{[30]}$ and (PPh)$_5$ were synthesized according to literature procedures. Zinc chloride was dried by refluxing in thionyl chloride.$^{[32]}$

$^1H$ and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance 300 or Bruker Avance 500 spectrometers and internally referenced to the residual proton resonances (for CDCl$_3$, $^1H$ at $\delta = 7.26$, $^{13}C\{^1H\}$ at $\delta = 77.16$; for CD$_2$Cl$_2$, $^1H$ at $\delta = 5.32$, $^{13}C\{^1H\}$ at $\delta = 53.84$; for THF-$d_8$, $^1H$ at $\delta = 3.58, 1.72$, $^{13}C\{^1H\}$ at $\delta = 67.21, 25.31$; for $C_6D_6$, $^1H$ at $\delta = 7.16$, $^{13}C\{^1H\}$ at $\delta = 128.06$; for DMF-$d_7$, $^1H$ at $\delta = 8.03, 2.92, 2.75$, $^{13}C\{^1H\}$ at $\delta = 163.15, 34.89, 29.76$. $^{33}$ $^{31}P\{^1H\}$ spectra were recorded on a Bruker Avance 300 or Bruker Avance 250 and externally referenced (85% H$_3$PO$_4$). The $^1H$ and $^{13}C$ resonance signals were assigned by means of 2D HSQC and HMBC experiments. Melting points were measured on samples in sealed capillaries on a Büchi M-560 melting point apparatus and are uncorrected. Elemental analyses were performed at the microanalysis laboratory of ETH Zürich.

Synthesis of the adduct $^{MeNH}NHC=PPh$ (1): A 50 mL round bottom flask was charged with (PPh)$_5$ (1.00 g, 1.85 mmol, 1.0 eq) and NaOEt (0.900 g, 9.36 mmol, 5.1 eq) and both were dissolved in THF (20 mL). To the stirring solution, 1,3-dimethylimidazolium iodide ([MeNHCH-H][II]) (2.07 g, 9.24 mmol, 5.0 eq) was added over the course of 10 minutes, causing the initially pale yellow solution to turn bright orange. The reaction was allowed to stir at 20 °C for 60 minutes. All volatiles were removed under reduced pressure and the residue was extracted into toluene, filtered over Celite, and the solution was concentrated to roughly 10% of the original volume. $n$-hexane (30 mL) was added and the orange precipitate was collected on a glass frit and dried under reduced pressure, yielding 1.80 g of $^{MeNH}NHC=PPh$ (95%) as an orange powder.
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Analysis for C$_{11}$H$_{13}$N$_{2}$P$_{1}$: Calculated: C = 64.70%, H = 6.42%, N = 13.72%. Found: C = 64.0%, H = 6.2%, N = 12.9%. MP: 185 °C. $^1$H NMR (300.1 MHz, C$_6$D$_6$, 293 K): δ = 7.63 (ddd, $^3$J$_{H,H}$ = 7.0 Hz, $^4$J$_{H,P}$ = 5.9 Hz, 2H; o-PhH), 7.09 (td, $^3$J$_{H,H}$ = 7.4 Hz, $^4$J$_{H,P}$ = 2.0 Hz, 2H; m-PhH), 6.95 (tt, $^3$J$_{H,H}$ = 7.3 Hz, $^4$J$_{H,H}$ = 1.2 Hz, $^5$J$_{H,P}$ = 1.2 Hz, 1H; p-PhH), 5.64 (s, 2H; NCH$_2$), 2.83 (d, $^4$J$_{H,P}$ = 0.8 Hz, 6H; NCH$_3$). $^{13}$C($^1$H) NMR (75.5 MHz, C$_6$D$_6$, 293 K): $^1$J$_{C,P}$ = 99.6 Hz; NCN), 147.0 (d, $^1$J$_{C,P}$ = 46.5 Hz; ipso-PhC), 133.4 (d, $^2$J$_{C,P}$ = 17.8 Hz; o-PhC), 127.5 (d, $^3$J$_{C,P}$ = 5.3 Hz; m-PhC), 122.9 (s; p-PhC), 119.0 (d, $^3$J$_{C,P}$ = 3.2 Hz; NCH), 36.2 (d, $^3$J$_{C,P}$ = 9.8 Hz; NCH$_3$). $^{31}$P($^1$H) NMR (121.5 MHz, C$_6$D$_6$, 293 K): δ = −49.1 (s).

Synthesis of the adduct $^{\text{Mes}}$NHC=PPh: A 50 mL round bottom flask was charged with (PPh)$_5$ (1.00 g, 1.85 mmol, 1.0 eq) and NaOtfBu (0.900 g, 9.36 mmol, 5.1 eq) and both were dissolved in THF (20 mL). To the stirring solution, $[^{\text{Mes}}$NHC-H]-[Cl]) (3.15 g, 9.24 mmol, 5.0 eq) was added over the course of 10 minutes, causing the initially pale yellow solution to turn bright orange. The reaction was allowed to stir at 20 °C for 60 minutes. All volatiles were removed under reduced pressure and the residue was extracted into toluene, filtered over Celite, and the solution was concentrated to roughly 10% of the original volume. n-hexane (30 mL) was added and the orange precipitate was collected on a glass frit and dried under reduced pressure, yielding 3.54 g of $^{\text{Mes}}$NHC=PPh (93%) as an orange powder. This sample was spectroscopically identical to a previously reported sample.$^{[12]}$

Synthesis of the adduct $^{\text{Dipp}}$NHC=PPh: A 50 mL round bottom flask was charged with (PPh)$_5$ (1.00 g, 1.85 mmol, 1.0 eq) and NaOtfBu (0.900 g, 9.36 mmol, 5.1 eq) and both were dissolved in THF (20 mL). To the stirring solution, $[^{\text{Dipp}}$NHC-H]-[Cl]) (3.93 g, 9.24 mmol, 5.0 eq) was added over the course of 10 minutes, causing the initially pale yellow solution to turn bright orange. The reaction was allowed to stir at 20 °C for 60 minutes. All volatiles were removed under reduced pressure and the residue was extracted into toluene, filtered over Celite, and the solution was concentrated to roughly 10% of the original volume. n-hexane (30 mL) was added and the orange precipitate was collected on a glass frit and dried under reduced pressure, yielding 3.99 g of $^{\text{Dipp}}$NHC=PPh (87%) as an orange powder. This sample was spectroscopically identical to a previously reported sample.$^{[10]}$
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Synthesis of bis(phosphinidene) zinc complex 2: A solution of ZnCl₂ (0.066 g, 0.484 mmol, 1.0 eq) in THF (2 mL) was added dropwise to a solution of Me₅NHC=PPh (0.200 g, 0.980 mmol, 2.0 eq) in THF (1 mL) and the reaction mixture was allowed to stir for 10 min. Next, the pale yellow precipitate was collected on a glass frit, washed with THF (2 mL) and dried in vacuo to give [Me₅NHC=PPh]₂ZnCl₂ (2) as a pale yellow solid (0.200 g, 0.366 mmol, 76%). Single crystals suitable for X-ray crystallography were obtained from the reaction mixture in DME at 20 °C.

MP: >200 °C (decomposition). Due to the poor solubility of 2 in common organic solvents its structure is only evidenced from X-ray crystallographic data (Scheme 2).

Synthesis of the phosphinidene zinc complex 3: A solution of Me₅NHC=PPh (1.00 g, 4.90 mmol, 1.0 eq) in DME (10 mL) was added dropwise to a suspension of ZnCl₂ (0.734 g, 5.35 mmol, 1.1 eq) in DME (60 mL). Upon vigorous stirring for 15 minutes, the initially yellow suspension turned colorless. Next, this suspension was filtered through a teflon cannula equipped with a glassfiber filter to remove the excess ZnCl₂ and the solution was left standing at 20 °C. The product that precipitated overnight was collected on a glass frit and dried under reduced pressure to yield 3 as a white powder (1.21 g). The filtrate was concentrated to roughly 10% of the original volume and cooled to −35 °C overnight. Collection of the precipitate on a glass frit and subsequent drying under reduced pressure afforded a second batch of 3 (0.250 g). Combined yield 87% (n=1, 1.46 g, 4.29 mmol). Single crystals suitable for X-ray crystallography were obtained from a saturated THF solution at −35 °C. One THF molecule completes Zn four-coordination in the crystal structure, however after drying in vacuo complex 3 does not contain any solvent coordinated; the following analyses were performed on the solvent-free product {Me₅NHC=PPhZnCl₂}ₙ, which is used in the synthesis of 4 and 10:

Analysis for C₁₁H₁₃Cl₂N₂P₂Zn₁: Calculated: C = 38.8%, H = 3.9%, N = 8.2%. Found: C = 38.3%, H = 3.9%, N = 7.9%. MP: >147 °C (decomposition). ¹H NMR (300.1 MHz, THF-d₈, 293K): δ = 7.54 (ddd, 3JₘH₂ = 6.6 Hz, 4H, ¹JₘH₄ = 1.4 Hz, 5JₘH₅ = 7.4 Hz, 2H; o-PhH), 7.38 (s, 2H; NCH₃), 7.16 (td, 3JₘH₂ = 7.1 Hz, 4JₘH₅ = 1.8 Hz, 2H; m-PhH), 7.12 (td, 3JₘH₂ = 7.0 Hz, 4JₘH₅ = 1.4 Hz, 1H; p-PhH), 3.60 (s, 6H; NC₃H₃). ¹³C{¹H} NMR (75.5 MHz, THF-d₈, 293 K): δ = 156.9 (d, ¹JₜC = 67.7 Hz; NCN), 136.6 (d, ¹JₜC = 18.0 Hz; ipso-PhC), 134.7 (d, ²JₜC = 14.2 Hz; o-PhC), 128.9 (d, ³JₜC = 5.0 Hz, m-PhC), 126.9 (s; p-PhC), 124.2 (d, ³JₜC = 1.5 Hz; NCH₃),
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37.6 (d, $^3J_{C,P} = 8.0$ Hz; NCH$_3$). $^{31}$P{$^1$H} NMR (121.5 MHz, THF-d$_6$, 293 K): $\delta = -88.1$ (s).

**Reaction of 2 with ZnCl$_2$:** In an NMR tube, ZnCl$_2$ powder (0.004 g, 0.029 mmol, 1.1 eq) was slowly added to a yellow suspension of 2 (0.015 g, 0.027 mmol, 1.0 eq) in THF (0.6 mL) at 20 °C. The resulting colorless solution was analyzed by $^{31}$P{$^1$H} NMR spectroscopy, indicating the formation of 3.

**Reactions of the phosphinidene zinc complex 3 with organic electrophiles**

Addition of organic electrophiles was performed to both in situ prepared $^{14}$MeNHC=Ph=PPh$_2$ZnCl$_2$ complex and isolated compound 3. Both methods lead to the same products, meanwhile requiring different amounts of solvent. Herein we report the optimal procedures for each electrophile.

**Reaction of the phosphinidene zinc complex 3 with 9,10-phenanthrenequinone:** A solution of 9,10-phenanthrenequinone (0.320 g, 1.54 mmol, 1.05 eq.) in THF (15 mL) was added dropwise to a solution of 3 ($n=1$, 0.500 mg, 1.47 mmol, 1.0 eq) in THF (25 mL) at −78 °C to give a green solution and a small amount of a yellow precipitate. The reaction mixture was stirred for 10 min, the precipitate filtered off and the filtrate evaporated to dryness. Extraction into toluene (3 x 10 mL) and recrystallization from toluene at 60 °C gave phosphonite 4 as a pale green crystalline solid in 46% yield (0.214 g, 0.677 mmol). Crystals suitable for X-ray crystallography were obtained from a saturated toluene solution at 20 °C. The residue, which was insoluble in toluene, contained $[^{14}$MeNHC-ZnCl$_2]_n$ together with some unidentified by-products.

**Analysis for C$_{20}$H$_{13}$O$_2$P:** Calculated: C = 76.0%, H = 4.1%, N = 0.0%. Found: C = 75.7%, H = 3.9%, N = 0.1%. **MP:** 142 °C. $^1$H NMR (300.1 MHz, C$_6$D$_{6}$, 293K): $\delta = 8.32$ (d, $^3J_{H,H} = 8.3$ Hz, 2H; o-C$_6$H$_4$), 8.21 (dd, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 0.9$ Hz, 2H; o-C$_6$H$_4$), 7.46 (t, $^3J_{H,H} = 6.6$ Hz, 2H; m-C$_6$H$_4$), 7.37 (t, $^3J_{H,H} = 7.5$ Hz, 2H; m-C$_6$H$_4$), 7.28 (ddd, $^3J_{H,H} = 6.6$ Hz, $^4J_{H,H} = 1.4$ Hz, $^3J_{H,P} = 7.9$ Hz, 2H; o-PPhH), 6.87-6.70 (m, 3H; m-PPhH, o-PPhH). $^{13}$C{$^1$H} NMR (75.5 MHz, CD$_2$Cl$_2$, 293 K): $\delta = 142.4$ (d, $^1J_{C,P} = 48.5$ Hz; ipso-PPhC), 138.2 (d, $^2J_{C,P} = 6.8$ Hz; ipso-phenanthreneOC), 131.9 (s; p-PPhC), 128.9 (d, $^3J_{C,P} = 6.5$ Hz; m-PPhC), 128.7 (d, $^2J_{C,P} = 23.4$ Hz; o-PPhC), 128.2 (s; ipso-phenanthreneC), 127.7 (s; m-C$_6$H$_4$), 125.9 (s; m-
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\[ C_6H_4 \), 123.7 (s; \textit{ipso}-phenanthreneC), 123.6 (s; \alpha-C_6H_4), 121.2 (s; \alpha-C_6H_4). \]

\[ ^{31}P\{^1H\} \text{NMR} \ (121.5 \text{ MHz}, C_6D_6, 293 \text{ K}): \delta = 183.3 (s). \]

Reaction of the phosphinidene zinc complex 3 with 2 equivalents of \textit{diphenylketene}: To a stirring solution of \( \text{MeNHC=PPh} \ (0.100 \text{ g}, 0.490 \text{ mmol, 1.0 eq}) \) in \( \text{THF} \) (4 mL), \( \text{ZnCl}_2 \ (0.070 \text{ g}, 0.514 \text{ mmol, 1.05 eq}) \) was added over the course of 5 minutes as a solid at 20 °C. The resulting colorless solution was stirred for 5 minutes after which \textit{diphenylketene} (0.200 g, 1.03 mmol, 2.1 eq) in \( \text{THF} \) (6 mL) was added dropwise. The reaction mixture was stirred for 10 min and the volatiles removed under reduced pressure. The residue was extracted into refluxing \( n \)-hexane (2 x 20 mL), giving a mixture of 6 and 7 in approximately 2:3 ratio (determined by the integration of the signals in the \( ^{31}P\{^1H\} \text{NMR} \) spectra). The \( ^{13}C \) and \( ^{31}P \) NMR signals of the heterocycle 7 correspond to literature values,\(^6\) while heterocycle 6 was identical to the one obtained in the reaction of \( \text{MeNHC=PPh} \) with \textit{diphenylketene} without \( \text{ZnCl}_2 \) (see below). The residue, which was insoluble in \( n \)-hexane, contained \( [\text{MeNHC-ZnCl}_2]_n \).

6: \( ^{31}P\{^1H\} \text{NMR} \ (121.5 \text{ MHz}, \text{THF-d}_8, 293 \text{ K}): \delta = -2.6 \text{ (s).} \)

7: \( ^{31}P\{^1H\} \text{NMR} \ (121.5 \text{ MHz}, \text{THF-d}_8, 293 \text{ K}): \delta = 90.9 \text{ (s).} \)

\[ ^{13}C\{^1H\} \text{NMR} \ (75.5 \text{ MHz, THF-d}_8, 293 \text{ K}): \delta = 157.1 \text{ (d, } ^2J_{C,P} = 11.9 \text{ Hz; OCO), 96.4 (s; Ph}_2C=CO_2). \]

From the mixture, these characteristic signals of 7 were identified; the other carbon signals overlap with the ones of 6.

Reaction of the phosphinidene zinc complex 3 with 1 equivalent of \textit{diphenylketene}: A solution of \textit{diphenylketene} (0.120 g, 0.618 mmol, 1.05 eq) in \( \text{THF} \) (2 mL) was added dropwise to a stirring solution of 3 (n=1, 0.200 g, 0.587 mmol, 1.0 eq) in \( \text{THF} \) (10 mL) at 20 °C. The resulting pale yellow solution was evaporated to dryness and the crude product was washed with toluene (2 x 10 mL) and diethyl ether (2 x 5 mL) to give 10 as an off-white powder in 82% yield (0.300 g, 0.480 mmol). Due to its extreme sensitivity, compound 10 could not be obtained analytically pure. Based on \( ^{31}P\{^1H\} \text{NMR spectroscopy, it contained traces of 3, and heterocycles 6 and 7 (Figure 2). Crystallization from DME at } -35 \text{ °C afforded single crystals suitable for X-ray diffraction.} \)

\[ ^{31}P\{^1H\} \text{NMR} \ (121.5 \text{ MHz, THF, 293 K}): \delta = -16.6 \text{ (s).} \]
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Figure 2. $^{31}$P($^1$H) NMR spectrum of 10 with structures of impurities.

Reaction of 10 with diphenylketene: To a stirring solution of 10 (0.100 g, 0.160 mmol, 1.0 eq) in THF (2 mL) diphenylketene (0.034 g, 0.176 mmol, 1.1 eq) in THF (1 mL) was added at 20 °C. The $^{31}$P($^1$H) NMR spectrum of the resulting yellow solution showed signals at –2.3 ppm and 91.1 ppm in a ratio of 2:3, corresponding to the heterocycles 6 and 7, confirming the intermediacy of 10 in the formation of 6 and 7.

Reaction of the phosphinidene zinc complex 3 with trans-chalcone. Synthesis of $[^{15}$MeNHC·ZnCl$_2$]$_n$ (5): To a stirring solution of MeNHC=PPh (0.500 g, 2.45 mmol, 1.0 eq) in THF (7 mL), ZnCl$_2$ (0.350 g, 2.57 mmol, 1.05 eq) was added as a solid over the course of 5 minutes. After stirring the resulting colorless solution for 5 minutes, trans-chalcone (0.535 g, 2.57 mmol, 1.05 eq) was added as a solid over a period of 5 minutes. The reaction mixture was stirred for another 10 minutes before it was cooled to –35 °C overnight. The resulting precipitate was collected on a glass frit, washed with diethyl ether (3 x 5 mL) and dried under reduce pressure to give $[^{15}$MeNHC-ZnCl$_2$]$_n$ as a white powder in 83% yield (0.470 g, 2.02 mmol). Crystallization from a saturated THF solution at 20 °C afforded single crystals suitable for X-ray diffraction.
**Analysis for \( \text{C}_2\text{H}_8\text{Cl}_2\text{N}_2\text{Zn} \):** Calculated: C = 25.8%, H = 3.5%, N = 12.1%. Found: C = 26.4%, H = 3.3%, N = 11.8%. **MP:** >260 °C (decomposition). \(^1\)H NMR (300.1 MHz, DMF-\(d_7\), 293K): \( \delta = 7.49 \) (s, 2H; NCH), 3.99 (s, 6H; NCH\(_3\)). \(^{13}\)C\{\(^1\)H\} NMR (75.5 MHz, DMF-\(d_7\), 293 K): \( \delta = 172.3 \) (s; NCN), 123.4 (s; NCH), 37.0 (s; NCH\(_3\)).

**Synthesis of oxo-3-phospholene 8:** After removal of [MeNHC·ZnCl\(_2\)]\(_n\), the filtrate was evaporated to dryness and the residue was dissolved in diethyl ether (3 x 15 mL) and filtered over Celite. Removal of the solvent under reduced pressure and subsequent recrystallization from toluene at 60 °C afforded 8 as a white, crystalline solid in 80% yield (0.620 g, 1.96 mmol). Crystals suitable for X-ray crystallography were grown from a saturated toluene solution at 20 °C.

**Analysis for \( \text{C}_{21}\text{H}_{17}\text{OP} \):** Calculated: C = 79.7%, H = 5.4%, N = 0.0%. Found: C = 78.8%, H = 5.2%, N = 0.1%. **MP:** 123–124 °C. \(^1\)H NMR (300.1 MHz, C\(_6\)D\(_6\), 293K): \( \delta = 7.73 \) (dd, \(^3\)J\(_{H,H} = 8.2\) Hz, \(^4\)J\(_{H,H} = 1.4\) Hz, 2H; o-CH=C(PhH)), 7.51–7.16 (m, 2H; o-P(PhH)), 7.26–6.93 (m, 11H; PhH), 5.47 (dd, \(^3\)J\(_{H,P} = 8.8\) Hz, \(^4\)J\(_{H,H} = 3.9\) Hz, 1H; CH=CPH), 4.08 (dd, \(^3\)J\(_{H,P} = 3.4\) Hz, \(^2\)J\(_{H,P} = 3.4\) Hz, 1H; PC\(_{HPh}\)). \(^{13}\)C\{\(^1\)H\} NMR (75.5 MHz, CD\(_2\)Cl\(_2\), 293 K): \( \delta = 159.5 \) (d, \(^2\)J\(_{C,P} = 12.6\) Hz; CH=CPH), 143.1 (d, \(^1\)J\(_{C,P} = 35.2\) Hz; ipso-P(C\(_6\)H\(_5\))), 142.5 (d, \(^2\)J\(_{C,P} = 18.9\) Hz; ipso-PCH(C\(_6\)H\(_5\))), 132.0 (s; ipso-CH=C(C\(_6\)H\(_5\))), 129.9 (s; C\(_{PhH}\)), 129.5 (s; C\(_{PhH}\)), 129.3 (d, \(^1\)J\(_{C,P} = 1.7\) Hz; C\(_{PhH}\)), 129.1 (s; p-CH=C(C\(_6\)H\(_5\))), 128.0 (d, \(^2\)J\(_{C,P} = 8.7\) Hz; o-P(C\(_6\)H\(_5\))), 127.8 (d, \(^3\)J\(_{C,P} = 5.4\) Hz; o-PCH(C\(_6\)H\(_5\))), 127.2 (d, \(^1\)J\(_{C,P} = 23.4\) Hz; C\(_{PhH}\)). \(^{31}\)P\{\(^1\)H\} NMR (121.5 MHz, C\(_6\)D\(_6\), 293 K): \( \delta = 133.9 \) (s).

**Screening of the reaction of different Lewis acids with \( \text{MeNHC=PPh} (1) \)**

**Reaction of 1 with ZnCl\(_2\):** In an NMR tube, ZnCl\(_2\) powder (0.007 g, 0.051 mmol, 1.1 eq) was slowly added to an orange solution of 1 (0.010 g, 0.049 mmol, 1.0 eq) in THF (0.6 mL) at 20 °C. The resulting colorless solution was analyzed by \(^{31}\)P\{\(^1\)H\} NMR spectroscopy (Figure 3), indicating formation of 3.
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Figure 3. $^{31}$P($^1$H) NMR spectrum recorded directly after mixing $^\text{Me}$NHC=PPh with ZnCl$_2$ in THF at RT.

**Reaction of 1 with MgCl$_2$:** In an NMR tube, MgCl$_2$ powder (0.005 g, 0.052 mmol, 1.1 eq) was slowly added to an orange solution of 1 (0.010 g, 0.049 mmol, 1.0 eq) in THF (0.6 mL) at 20 °C. The resulting yellow suspension was analyzed by $^{31}$P($^1$H) NMR spectroscopy. The obtained spectrum is presented in Figure 4.

Figure 4. $^{31}$P($^1$H) NMR spectrum recorded directly after mixing $^\text{Me}$NHC=PPh with MgCl$_2$ in THF at RT.
The main signal (δ = −52.05 ppm; Figure 4) in the spectrum originates from unreacted \textsuperscript{Me}NHC\textsubscript{4}PPh, which is due to the poor solubility of MgCl\textsubscript{2} in THF. However, new products are also formed. The signals could be assigned by comparison with literature values\textsuperscript{[13]} to (PPh)\textsubscript{5} (m, δ = −5 to −6 ppm), (PPh)\textsubscript{6} (δ = −22.7 ppm), (PPh)\textsubscript{4} (δ = −48.3 ppm).

**Reaction of 1 with AlCl\textsubscript{3}:** In an NMR tube, AlCl\textsubscript{3} powder (0.014 g, 0.052 mmol, 1.1 eq) was slowly added to an orange solution of 1 (0.010 g, 0.049 mmol, 1.0 eq) in THF (0.6 mL) at 20 °C. The resulting colorless solution was analyzed by \textsuperscript{31}P\{\textsuperscript{1}H\} NMR spectroscopy (Figure 5), indicating the formation of (PPh)\textsubscript{5}, (PPh)\textsubscript{6}, (PPh)\textsubscript{4} and (PPh)\textsubscript{3}\textsuperscript{[34]}

![Figure 5. \textsuperscript{31}P\{\textsuperscript{1}H\} NMR spectrum recorded directly after mixing \textsuperscript{Me}NHC\textsubscript{4}PPh with AlCl\textsubscript{3} in THF at RT.]

**Reaction of 1 with BPh\textsubscript{3}:** In an NMR tube, BPh\textsubscript{3} powder (0.013 g, 0.054 mmol, 1.1 eq) was slowly added to an orange solution of 1 (0.010 g, 0.049 mmol, 1.0 eq) in THF (0.6 mL) at 20 °C. The resulting yellowish suspension was analyzed by \textsuperscript{31}P\{\textsuperscript{1}H\} NMR spectroscopy (Figure 6), indicating the formation of (PPh)\textsubscript{5}, (PPh)\textsubscript{4} and new product (δ = −36.2 ppm) assigned to the Lewis adduct \textsuperscript{Me}MHC\textsubscript{4}P(Ph)BPh\textsubscript{3}. After 1 h, however, the signal at −36.2 ppm disappeared, and only signals corresponding to cyclopolyphosphines and unreacted 1 were found in the spectrum (Figure 7).
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Figure 6. $^{31}\text{P}({}^1\text{H})$ NMR spectrum recorded directly after mixing $^{15}\text{N}$HNC=PPh with BPh$_3$ in THF at RT.

Figure 7. $^{31}\text{P}({}^1\text{H})$ NMR spectrum recorded after 1h after mixing $^{15}\text{N}$HNC=PPh with BPh$_3$ in THF at RT.

**Reaction of 1 with Zn(OAc)$_2$:** In an NMR tube, Zn(OAc)$_2$ powder (0.010 g, 0.054 mmol, 1.1 eq) was slowly added to an orange solution of 1 (0.010 g, 0.049 mmol, 1.0 eq) in THF (0.6 mL) at 20 °C. The resulting yellow suspension was analyzed by $^{31}\text{P}({}^1\text{H})$ NMR spectroscopy (Figure 8), indicating the formation of (PPh)$_5$, (PPh)$_6$, (PPh)$_4$ and an unidentified product (br, $\delta = -60.7$).
Reactions of $^{Me}$NHC=PPh with organic electrophiles

The reactivity of 1 towards electron-poor heterodiienes was also studied (Scheme 10). The substrates revealed diverse reactivity, albeit of low selectivity, likely due to the highly reactive free carbene being released. The reaction of 1 with two equivalents of 9,10-phenanthrenequinone resulted in formation of the dioxyphosphineoxide 11 and the quinone-methide 12. Addition of trans-chalcone to 1 led to an intractable mixture of products, among which the oxo-3-phospholene 8 was also formed in low yield. In fact, the desired phosphinidene transfer was only observed in the case of diphenylketene. However, together with the formation of the 1,3-oxaphospholan-5-one 6 as the sole phosphorus-containing product, the additional equivalent of ketene was consumed to trap the carbene to the carbene-ketene adduct 13.
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Scheme 10. Reactivity of $^{16}$Me,NHC=PPh (1) towards ortho-quinone, diphenylketene and trans-chalcone.

Figure 9. Molecular structures of 11 (disordered THF solvent molecules omitted), 12 (THF solvent molecule omitted, one crystallographic independent molecule is shown) and 13 (one crystallographic independent molecule is shown). Selected bond lengths [Å] and angles [°] for 11 (values for the second molecule in square brackets): P1–C1 1.7699(14), P1–O1 1.4598(10), P1–O2 1.6245(11), P1–O3 1.6251(10), C7–C8 1.3459(19); 12: N1–C1 1.353(2) [1.351(2)], N2–C1 1.3470(19) [1.3502(19)], C1–C6 1.460(2) [1.459(2)], C6–C7 1.406(2) [1.408(2)], C7–O1 1.2733(17) [1.2741(17)]; 13: N1–C1 1.3458(17) [1.3429(18)], N2–C1 1.3418(17) [1.3460(18)], C1–C6 1.5009(19) [1.507(2)], C6–O1 1.2889(16) [1.2852(17)], C6–C7 1.3768(19) [1.381(2)].
Reaction of $^{Me}_{NHC}=PPh$ with phenanthrene-9,10-quinone. Synthesis of quinone-methide 12: To a stirring solution of $^{Me}_{NHC}=PPh$ (0.200 g, 0.980 mmol, 1.0 eq) in THF (8 mL) was added phenanthrene-9,10-quinone (0.410 g, 1.970 mmol, 2.0 eq) as a solid over the course of 20 minutes at 20 °C. Next, the solution was cooled to −35 °C overnight, which resulted in the precipitation of 12. The precipitate was collected on a glass frit, washed with THF (2 mL) and dried under reduced pressure, yielding light orange crystals of 12 (0.268 g, 0.930 mmol, 95%). The compound co-crystallizes with half an equivalent of THF. Crystals suitable for single-crystal X-ray crystallography were obtained from THF at −35 °C (Figure 9).

Analysis for C$_{42}$H$_{40}$N$_4$O$_3$: Calculated: C = 77.75%, H = 6.21%, N = 8.64%. Found: C = 77.75%, H = 6.07% N = 8.48%. MP: >220 °C (decomposition). $^1$H NMR (300.1 MHz, CD$_2$Cl$_2$, 293K): $\delta$ = 8.55 (dd, $^3$J$_{H,H}$ = 7.9 Hz, $^4$J$_{H,H}$ = 1.6 Hz, 1H; o-C$_6$H$_4$), 8.51 (dd, $^3$J$_{H,H}$ = 8.2 Hz, $^4$J$_{H,H}$ = 0.4 Hz, 1H; o-C$_6$H$_4$), 8.42 (dd, $^3$J$_{H,H}$ = 8.1 Hz, $^4$J$_{H,H}$ = 0.6 Hz, 1H; o-C$_6$H$_4$), 7.63 (ddd, $^3$J$_{H,H}$ = 8.3 Hz, $^4$J$_{H,H}$ = 7.0 Hz, $^4$J$_{H,H}$ = 1.6 Hz, 1H; m-C$_6$H$_4$), 7.52 (ddd, $^3$J$_{H,H}$ = 8.0 Hz, $^3$J$_{H,H}$ = 7.0 Hz, $^4$J$_{H,H}$ = 1.2 Hz, 1H; m-C$_6$H$_4$), 7.26 (s, 2H; HC=CH), 7.25 (ddd, $^3$J$_{H,H}$ = 8.0 Hz, $^3$J$_{H,H}$ = 7.0 Hz, $^4$J$_{H,H}$ = 1.3 Hz, 1H; m-C$_6$H$_4$), 7.07 (ddd, $^3$J$_{H,H}$ = 8.2 Hz, $^3$J$_{H,H}$ = 7.0 Hz, $^4$J$_{H,H}$ = 1.2 Hz, 1H; m-C$_6$H$_4$), 6.51 (dd, $^3$J$_{H,H}$ = 8.1 Hz, $^4$J$_{H,H}$ = 0.8 Hz, 1H; o-C$_6$H$_4$), 3.65 (s, 6H; NCH$_3$). $^{13}$C($^1$H) NMR (CDCl$_3$): $\delta$ = 186.86 (s; C=O), 150.60, 134.48, 133.46, 132.70, 127.82, 126.93, 125.51, 125.43, 121.85, 120.83, 118.79, 118.37, 88.99, 35.11 (s; CH$_3$).

Synthesis of dioxyphosphineoxide 11: After removal of 12, the volume of the filtrate was reduced to approximately 3 mL and the solution was cooled to −35 °C for 24 hours. The crystalline precipitate was collected on a glass frit and dried under reduced pressure to yield 11 as a pale green solid in 84% yield (0.275 g, 0.828 mmol).

Analysis for C$_{20}$H$_{10}$O$_3$P$_3$: Calculated: C = 72.29%, H = 3.94%. Found: C = 72.22%, H = 3.79%. MP: 184–187 ºC. $^1$H NMR (300.1 MHz, CD$_2$Cl$_2$, 293K): $\delta$ = 8.79–8.72 (m, 2H; o-phenanthreneH), 8.12–8.05 (m, 2H; o-phenanthreneH), 7.92 (ddd, $^3$J$_{H,P}$ = 14.9 Hz, $^3$J$_{H,H}$ = 7.2 Hz, $^4$J$_{H,H}$ = 1.4 Hz, 2H; o-PPhH), 7.76–7.67 (m, 5H; m-phenanthreneH, p-PPhH), 7.55 (td, $^3$J$_{H,H}$ = 7.8, $^4$J$_{H,P}$ = 5.1 Hz, 2H; m-PPhH). $^{13}$C($^1$H) NMR (75.5 MHz, CD$_2$Cl$_2$, 293K): $\delta$ = 137.4 (d, $^1$J$_{C,P}$ = 0.9 Hz; ipso-phenanthreneC), 135.1 (d, $^1$J$_{C,P}$ = 3.3 Hz, p-PPhC), 132.9 (d, $^2$J$_{C,P}$ = 11.7 Hz; o-PPhC), 129.5 (d, $^3$J$_{C,P}$ = 16.5 Hz; m-PPhC), 128.2 (s; m-phenanthreneH), 128.1 (s; ipso-phenanthreneC), 126.8 (s; m-phenanthreneC), 126.3 (br. s., ipso-PPhC), 123.8 (s; o-phenanthreneC), 122.0 (d, $^1$J$_{C,P}$ = 8.9 Hz; ipso-phenanthreneC), 121.1 (s; o-
phenanthrene). $^{31}P(^1H)$ NMR (121.5 MHz, CD$_2$Cl$_2$, 293 K): $\delta = 38.6$ (s).

**Reaction of $^{13}$NHC=PPh with diphenylketene.** Synthesis of carbene-ketene adduct 13: A solution of diphenylketene (0.310 g, 1.60 mmol, 3.1 eq) in THF (2 mL) was slowly added to a stirring solution of $^{13}$NHC=PPh (0.100 g, 0.490 mmol, 1.0 eq) in THF (3 mL). The reaction mixture was stirred for 1 hour at 20 °C and then cooled to −35 °C for 16 hours. The yellow-green precipitate was collected on a glass frit, washed with THF (2 mL) at −20 °C and dried under reduced pressure yielding a light green powder of 13 (0.100 g, 0.344 mmol, 70%).

![Diagram](13)

**Synthesis of 1,3-oxaphospholane-5-one 6:** Next, the filtrate was evaporated to dryness, the brown residue extracted into refluxing n-hexane (3 x 20 mL) and filtered through a teflon cannula equipped with a glassfiber filter. Concentration to roughly 20% of the original volume and cooling to −35 °C afforded 6 as a white crystalline solid in 83% yield (202.2 mg, 0.407 mmol). Crystals suitable for single-crystal X-ray crystallography were obtained from diethyl ether at 20 °C.

**Analysis for C$_{34}$H$_{25}$O$_2$P$_1$:** Calculated: C = 82.2%, H = 5.1%, N = 0.0%. Found: C = 82.0%, H = 4.9%, N = 0.1%. MP: 167–168 °C. $^1$H NMR (300.0 MHz, CDCl$_3$, 293K): $\delta = 7.73$ (dd, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 2.2$, 2H; o-Ph$H$), 7.51–6.95 (m, 21H; Ph$H$), 6.75 (d, $^3J_{HH} = 7.2$ Hz, 2H; o-Ph$H$). $^{13}$C($^1$H) NMR (75.5 MHz, CDCl$_3$, 293K): $\delta = 174.1$ (d, $^2J_{CP} = 3.5$ Hz; C=O), 143.8 (d, $^1J_{CP} = 23.2$ Hz; P=PCPh$_2$), 139.5 (d, $^1J_{CP} = 2.3$ Hz; C$_{o}$), 139.4 (d, $^1J_{CP} = 8.7$ Hz; C$_{o}$), 138.1 (d, $^1J_{CP} = 3.7$ Hz; C$_{o}$), 137.7 (d, $^1J_{CP} = 4.4$ Hz; C$_{o}$), 135.1 (d, $^1J_{CP} = 20.7$ Hz; C$_{o}$), 135.6 (d, $^1J_{CP} = 19.0$ Hz; C$_{phH}$), 132.5 (d, $^1J_{CP} = 21.3$ Hz; C$_{o}$) 130.2 (s; C$_{phH}$), 130.2 (d, $^1J_{CP} = 9.5$ Hz; C$_{phH}$), 129.4 (d, $^1J_{CP} = 1.7$ Hz; C$_{phH}$), 129.3 (d, $^1J_{CP} = 7.1$ Hz; C$_{phH}$), 129.2 (d, $^1J_{CP} = 17.3$ Hz; C$_{phH}$), 128.9 (d, $^1J_{CP} = 1.7$ Hz; C$_{phH}$), 128.7 (d, $^1J_{CP} = 21.6$ Hz; C$_{phH}$), 128.6 (d, $^1J_{CP} = 15.0$ Hz; C$_{phH}$), 128.0 (s), 126.9 (d, $^1J_{CP} = 1.3$ Hz; C$_{phH}$), 62.7 (d, $^1J_{CP} = 15.2$ Hz; P=PCPh$_2$). $^{31}$P($^1$H) NMR (121.5 MHz, CD$_2$Cl$_2$, 293 K): $\delta = 0.0$ (s).
**Chapter 2**

**Reaction of $^{15}$MeNHC=PPh with trans-chalcone:** A solution of trans-chalcone (0.428 g, 2.06 mmol, 2.1 eq) in THF (8 mL) was slowly added to a stirring solution of $^{15}$MeNHC=PPh (0.200 g, 0.979 mmol, 1.0 eq) in THF (5 mL) at $-78^\circ$C to give a dark green suspension. The reaction mixture was stirred for 2 hours at 20 $^\circ$C and was analyzed using $^{31}$P NMR spectroscopy (see Figure 10). Since the spectrum still contained the signal corresponding to starting material ($\delta = -51.4$ (16.33%)), an additional equivalent of trans-chalcone (0.204 g, 0.979 mmol, 1 eq) was added as a solid. The resulting reaction mixture was stirred for 2 hours and again was analyzed by $^{31}$P NMR spectroscopy (see Figure 11). The spectrum shows formation of 8 ($\delta = 133.9$ (39.56%)) together with some unidentified products ($\delta = 135.7$ (23.80%), 135.6 (23.80%), 126.1 (5.08%), 42.7 (3.61%), 32.3 (4.15%)), but it was impossible to purify the compounds from the mixture. However, single crystals of 8 were obtained from the mixture and confirmed the identity of this phosphorus heterocycle. In addition, low quality single crystals of 14 were obtained from the precipitation and allowed us to identify 14 as the zwitterionic carbene-chalcone species.

![Figure 10. $^{31}$P($^1$H) NMR spectrum recorded after mixing $^{15}$MeNHC=PPh with trans-chalcone (2.1 eq.).](image-url)
Figure 11. $^{31}$P($^1$H) NMR spectrum recorded after mixing $^{15}$NHC=PPh with trans-chalcone (3.1 eq.)

**X-ray structure determination**

Single crystals suitable for X-ray diffraction were coated with Polybutene oil ($M_\text{w} \approx 920$ g mol$^{-1}$) in a glovebox and transferred to a Nylon loop. Diffraction studies were performed on an *Rigaku Oxford Diffraction* XCalibur S or a *Bruker* X8 APEX2 diffractometer, both equipped with a molybdenum X-ray tube ($\lambda = 0.7107 \text{ Å}$). Preliminary data was collected to determine the crystal system. The data was processed using the corresponding diffractometer software (CrysAlisPro v38.41 and Apex2 v.2014.1) and corrected for absorption with a multi-scan method.

The structures were solved using direct methods (ShelXS) or intrinsic phasing (ShelXT) and refined using least square procedures (ShelXL) on Olex2 v1.2.8.

CCDC 923521 (1), 1523933 (2), 1523907 (3), 1523934 (4), 1523939 (5), 1523936 (6), 1523935 (8) and 1523941 (10) contain the supplementary crystallographic data for this chapter. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
2.6 References and Notes


[8] CCDC 923521 (1), 1523933 (2), 1523907 (3), 1523934 (4), 1523939 (5), 1523936 (6), 1523935 (8) and 1523941 (10) contain the supplementary crystallographic data for this chapter. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.


[14] See Sections 2.4 and 2.5 for further details.


[16] Typical alkynes, alkenes and dienes did not exhibit any reactivity toward 3. We have also investigated the reactions of [MeNHC=PPh] (1) directly with organic electrophiles, see Section 2.5 for details.


Facile Phenylphosphinidene Transfer Reactions from Carbene-Phosphinidene Zinc Complexes


[21] Derivatives of 6 and 7 have been shown to catalyse the 1,4-diboration of 1,3-dienes, see: C. H. Schuster, B. Li, J. P. Morken *Angew. Chem. Int. Ed.* **2011**, *50*, 7906–7909.


[35] CCDC 1523938 (11), 1523940 (12) and 1523937 (13) contain the supplementary crystallographic data for this chapter. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.