CPh3 as a functional group in P-heterocyclic chemistry: elimination of HCPh3 in the reaction of P-CPh3 substituted Li/Cl phosphinidenoid complexes with Ph2C=O

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CPh₃ as a functional group in P-heterocyclic chemistry: elimination of HCPH₃ in the reaction of P-CPh₃ substituted Li/Cl phosphinidenoid complexes with Ph₂C=O

C. Murcia García, a A. Espinosa Feroa, a,b G. Schnakenburg a and R. Streubel, a,*

P-CPh₃ substituted oxaphosphirane complexes 3 were prepared using Li/Cl phosphinidenoid complexes 2 (M = Cr, Mo, W) and benzaldehyde. Employing 2 and benzophenone resulted in the formation of oxaphospholane complexes 4 and 5, the former bearing a benzo-c-1,2-oxaphospholane and the latter a novel pentacyclic P-ligand. According to DFT studies the latter P-heterocycle arises from formal dimerization of a transient benzo-fused 2-phosphafurane complex 8, one of the fragments undergoing water-catalyzed [1,3]H shift (4) and the other (11) formed via elimination of HCPh₃.

Introduction

The ability to stabilize a negative or positive charge, or a radical centre makes the triphenylmethyl group (CPh₃ or “trityl”) unique, and came first to the fore through the seminal work of Gomberg.1 It should be also noted that the bulkiness of the trityl group combined with the aforementioned abilities has attracted interest in main group element chemistry: Schmutzler et al. introduced the trityl group into organophosphorus chemistry.2 For example, he demonstrated that this group enables access to a wide variety of very reactive and/or unstable compounds, for example, acyclic diphosphaurea derivatives3, 1,3-diphosphetane-2,4-dione, acyl(chloro)organophosphanes,4 and more.5 Grützmacher et al. had recognized the synthetic potential for low-coordinate phosphorus compounds and reported on the C-trityl phosphalkyne.6 In a preliminary study Schmutzler showed that trityl can serve as a leaving group if such phoshane derivatives are treated with very strong acids.7

On the other hand, we recently demonstrated that the accessibility of transition-metal oxaphosphirane complexes was hugely facilitated due to the availability of Li/Cl phosphinidenoid complexes.8 Of particular importance was the first derivative bearing the sterically demanding trityl group at phosphorus,8d being stable at ambient temperature for some hours. It is remarkable that self-condensation/elimination processes, observed before for less demanding substituents, is effectively suppressed. Recent computational studies stressed the reactivity-determining key role of P-trityl groups in three-membered phosphorus heterocycles.9 To date only a few coordination compounds of P-trityl substituted phosphane complexes have been published.10 One result deserves special attention as a transiently formed P-trityl derivative had displayed a remarkable reactivity: one of the phenyl rings of the CPh₃ group acted as a diene source in an intramolecular Diels-Alder reaction.11

Herein, the synthesis of P-trityl substituted oxaphosphirane complexes 3a,b as well as the products of the reaction of Li/Ci phosphinidenoid complexes 2a-c with benzophenone is reported. The latter constitutes the first molecular evidence of the loss of the trityl entity in P-heterocyclic chemistry and could be also key for the synthesis of P-functionalized oxaphosphirane complexes.

Results and discussion

Synthesis

To broaden the scope of the study, Li/Cl phosphinidenoid complexes 2a-c (Scheme 1) were first synthesized using a protocol for chlorine/lithium exchange in complexes 1a-c,8d initially developed for 1c/2c.8d

Scheme 1. Synthesis of P-CPh₃ phosphinidenoid complexes 2a-c.

Reaction of Li/Cl phosphinidenoid complexes 2a,b,c8d with benzaldehyde led to the clean formation of oxaphosphirane derivatives 3a,b,c8d (Scheme 2) which were fully characterized.
by means of NMR, mass spectrometry as well as X-ray analysis (see ESI for 3a,b).

Scheme 2. Synthesis of P-CPh₃ oxaphosphirane complexes 3a-c and complexes 4d-f and 5d-f derived from benzophenone.

In order to investigate the effect of the expected ring strain energy increase of the oxaphosphirane ring imposed by two phenyl substituents on the heterocycle and the P-CPh₃ group, compounds 2a-c were reacted with benzophenone. To our great surprise, the ³¹P{¹H} NMR spectra showed no oxaphosphirane complexes, but two unexpected products 4d-f and 5d-f, 4d-f being the major products (Table 1). To get further insights ³¹P{¹H} NMR monitoring of the reactions were performed (-78 to 25 °C), but oxaphosphirane complexes could not be detected. The ³¹P{¹H} NMR spectra showed singlets for complexes 4d-f, whereas AB-type spin systems appeared for the distinctly different phosphorus nuclei of 5d-f, all signals appeared as doublets with a \( J_{P,P} \) coupling of 3.8 Hz.

Based on the higher selectivity in case of chromium (d) and tungsten (f), these complexes were chosen to attempt separation by low temperature column chromatography, but without success. Despite this, the selective extraction of 4f could be achieved and the constitution was finally confirmed by X-ray crystallography (Figure 1), revealing the presence of a bicyclic 1,2-oxaphospholane ligand in complex 4f.

Table 1. ³¹P{¹H}NMR data (δ [ppm], and \( J_{P,P} \) [Hz]) of 3a-c, 4d-f, 5d-f and 4:5 ratios in THF solution.

<table>
<thead>
<tr>
<th>Metal</th>
<th>3a-c</th>
<th>4d-f</th>
<th>5d-f</th>
<th>( J_{P,P} )</th>
<th>Ratio 4:5</th>
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<tr>
<td>Cr</td>
<td>58.7</td>
<td>190.3</td>
<td>210.5/165.6</td>
<td>3.8</td>
<td>5:1</td>
</tr>
<tr>
<td>Mo</td>
<td>33.4</td>
<td>167.4</td>
<td>186.3/138.2</td>
<td>3.8</td>
<td>5:3</td>
</tr>
<tr>
<td>W</td>
<td>16.0</td>
<td>145.1</td>
<td>164.4/112.3</td>
<td>3.8</td>
<td>5:1</td>
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Although several attempts to separate 5e from 4e via column chromatography were also unsuccessful, the better ratio of 4e:5e (see Table 1) enabled to get single crystals of the latter from diethyl ether at -30 °C. The X-ray structure of the pentacyclic complex 5e (Figure 2) surprisingly showed (formally) two units of Ph₂CO, but only one belonging to a complete (opened) oxaphosphirane unit. In the other P-containing part, only a partial oxaphosphirane complex can be (formally) identified, but without a HCP₃ moiety. All bond lengths and angles in 5e are in the expected range except, e.g. P1-Mo1 (2.4258 Å), but which is significantly shorter than P2-Mo2 (2.5259 Å). The five-membered ring containing P2 is roughly planar (distance of O7 to the P2-C14-C15-C25 mean plane, 0.108 Å due to the double bond between C15 and C25 (Figure 2).
reaction of phosphinidenoid complex to the benzylic position in diastereomer complexes (relative energy of formation of the corresponding oxaphosphirane complex was comparison with previous reports.

Tungsten complexes were used as models to enable comparison with previous reports\textsuperscript{12} and in agreement with them, formation of the corresponding oxaphosphirane complex was assumed as first product in the reaction of Li/Cl phosphinidenoid complexes with carbonyl compounds, although simple substitution of Cl by O at P could also be envisaged (vide infra). According to the above mentioned report, monoaryl substituted oxaphosphirane complex \textit{3g} preferentially undergoes exergonic (-6.57 kcal/mol) C-O bond cleavage with a moderate energy barrier 28.91 kcal/mol), leading to a \textit{side-on} phosphaalkene \textit{P}-oxide complex \textit{4g}. In contrast, a higher barrier P-C bond cleavage path (37.72 kcal/mol) being rather endergonic (+28.90 kcal/mol) affords \textit{7g}. In case of the diphenyl model system \textit{3h}, both processes have a lower barrier (Figure 3), the P-C bond cleavage product \textit{7h} being comparatively stabilized with respect to \textit{7g} due to extensive delocalization of the positive charge. In stark contrast, the C-O cleavage product \textit{6h} is destabilized presumably due to steric reasons.

![Scheme 3](image)

\textbf{Scheme 3.} Mechanistic proposal for the formation of \textit{4h}.

Therefore, the C-O bond cleavage equilibrium for \textit{3h} is expected to be shifted to the rather reactive (more slowly formed) P-C bond cleavage product \textit{7h} which readily undergoes cyclization by attack of the nucleophilic P atom at the closest phenyl ortho position, thus giving rise to bicyclic derivative \textit{8h}. Complex \textit{7h} exists as two conformers, differing in the helical orientation of the \textit{Ph}_{\text{P}}C^{-}\textit{ moiety, the most unstable of which (\textit{7h}')} cyclizes to the most stable diastereomer of the bicyclic complex \textit{8h}'; whereas the other helical isomer \textit{7h} gives rise to less stable diastereomer \textit{8h}'. Worth mentioning is that oxaphosphirane complex \textit{3} might not be formed in real systems due to steric congestion and, alternatively, ylide complex \textit{7} could directly result upon reaction of phosphinidenoid complex \textit{2} with benzophenone and evolve towards the five-membered derivative \textit{8h}.

Formation of the final (model) complex \textit{4h}, whose comparative stability arises from the gain of aromatic character in the benzo-fused ring, could be explained through \textit{supra} \textit{[1,3]H} shift to the benzylic position in diastereomer \textit{8h}'. According to Woodward-Hoffmann orbital symmetry rules\textsuperscript{13}, this process is thermally forbidden and displays a high energy barrier.\textsuperscript{14} In order to explain the formation of \textit{4} through a lower energy process, the assistance of a molecule having hydrogen bond (HB) donor and acceptor sites might be assumed, therefore acting as a catalyst for the H-shift \textit{8h'}→\textit{4h} rearrangement. A water molecule has been used as model for such a catalytic species (vide infra),\textsuperscript{16} although any other proton carrier species present in the reaction medium could similarly account for the catalyzed proton transfer. Thus \textit{8h}'\cdot\textit{2H}_{2}\text{O} was found to isomerize to \textit{4h}\cdot\text{H}_{2}\text{O} (Scheme 4) through a much lower yet significantly high pericyclic transition state (\textit{ΔΔE}_{\text{ZPE}} = 42.30 kcal/mol) (Figure 3)\textsuperscript{17} with thermal symmetry-allowed nature. The occurrence of two water molecules involved in the H transfer process further decreases the energy barrier of the rate-limiting first step (\textit{ΔΔE}_{\text{ZPE}} = 28.79 kcal/mol) which leads to a dihydrated zwitterion \textit{9h}·\textit{2H}_{2}\text{O} (Scheme 4), whose almost barrierless (water-mediated) O-to-C \textit{[1,2]H} shift affords the final model product \textit{4h}·\text{H}_{2}\text{O}.
The alternative two-step proton transfer through zwitierionic complex 8 requires elimination of the P-trityl substituent in complex 8 (studied at a somewhat lower computational level B for the molybdenum complex, see the Computational Details and SI) requires relative cis orientation of the H atom and the trityl group in 8e. This in turn enables a pericyclic phosphaene reaction affording diphenylmethyldicyclohexadiene 12 as by-product (Scheme 5). The latter can then isomerize to the more stable donor and acceptor species (vide supra), although in a non-catalytic fashion.

The alternative two-step proton transfer through zwitierionic complex 10e followed by P-group detachment constitutes a lower energy sequence to 11e. The resulting non-aromatic (i.e. reactive) bicyclic 2-phosphafuran complex intermediate 11e features a cyclic, conformationally s-cis locked phosphadiene character and, therefore, can be expected to behave as 4n-component and undergo a phospha-Diels-Alder reaction. The 2n component is the central double bond of the triene moiety in 8e', the diastereomer which cannot undergo trityl group elimination due to its relative trans orientation of the H atom at the ring junction. The regioselectivity of the [4+2] cycloaddition reaction might tentatively arise from i) π-stacking between the two phenyl rings that not only guides the approach of the two components but also stabilizes the final adduct and ii) the steric demand of the metal fragment in 11e hampering the approach to the phenyl substituent side in 8e'.

**Experimental**

**Analytical methods**

**Mass spectrometry**: Electron ionization (70eV) mass spectra were recorded on a Kratos MS 50 or on a MAT 95XL Finnigan spectrometer.

**NMR spectra** were recorded on a Bruker AX 300 spectrometer (1H: 300.1 MHz, 13C: 75.0 MHz and 31P: 121.5 MHz) using CDCl3 as solvent; shifts are given in ppm relative to external tetramethylsilane (1H, 13C) and 85% H3PO4 (31P).

**Elementary analysis**: Elemental analyses were performed using an elementary Vario EL analytical gas chromatograph.

**Single-crystal structure analysis**: Crystal structures were recorded on a Nonius Kappa CCD diffractometer and a Nonius MACH3 diffractometer. The structures were solved by Patterson methods or Direct Methods (SHELXS-97) and refined by full-matrix least squares on F2 (SHELXL-97). All non-hydrogens were refined anisotropically. Hydrogen atoms were included isotropically using the riding model on the bound atoms; in some (denoted) cases hydrogen atoms were located in the Fourier difference electron density. Absorption corrections were carried out analytically or semi-empirically from equivalents. Additionally, some calculation of bond lengths and angles were obtained using the Ortep32 program.

**Preparative methods**

All reactions and manipulations were carried out under an atmosphere of dry argon, using Schlenk and vacuum line techniques. Argon was cleaned over a BTS catalyst; the drying of the Ar gas occurred via silica gel and P2O5. Solvents were dried according to standard procedures and stored in brown glasses over sodium wire, and under inert gas atmosphere.

**Synthesis of [Li(12-crown-4)(THF)][(OC)8Cr(Ph3P=PCl)] (2a) for the spectroscopic characterization (2a)**

250 mg (0.47 mmol) of [(Ph3PCl)2Cr(CO)5] were dissolved in THF-d8 (5 mL) and 75 μL (1eq.) of 12-crown-4, in the following written as 12-c-4, were added. The solution was then cooled to -80 °C and 1.2 eq. of 8BuLi [1.7 M in n-pentane] were given dropwise and the solution was stir-red 5 minutes. After that, the solution was transferred into a cooled (-90°C) NMR tube via double needle. The Li/Cl phosphinidenoid chromium complex is much more stable than the molybdenum or...
tungsten derivative. Its full NMR characterization was performed after 4 hours at room temperature.

2a: Deep red solution. \(^1^H\) NMR (THF-d8) \(\delta = 3.74\) (s, 16H, 12-c-4), 6.9-7.5 (m, 15H, CPh), \(^1^3^C\) (H)NMR (THF-d8)66.9 (d, \(J_{CP} = 22.8\) Hz, CP), 68.3 (s, 12-c-4), 125.1 (s, para-Ph), 125.5 (d, \(J_{CP} = 1.3\) Hz, para-Ph), 125.9 (s, para-Ph), 127.1 (s, meta-Ph), 127.5 (s, meta-Ph), 128.0 (s, meta-Ph), 130.2 (d, \(J_{CP} = 15.7\) Hz, ortho-Ph), 131.1 (s, ortho-Ph), 131.7 (d, \(J_{CP} = 5.7\) Hz, ortho-Ph), 220.6 (d, \(J_{CP} = 6.9\) Hz, cis-CO), 221.6 (d, \(J_{CP} = 20.1\) Hz, trans-CO).

MS: selected data m/z (%) 572.0 [M]+, 432.1 (30) [M-SO], 326.0 (15) [M–SO-C,H\(_2\)O], 243.1 (100) [CPh\(_3\)].

Synthesis of [(OC)\(_2\)Mo(Ph\(_3\))COPC(H)Ph)] (3b)

To a freshly generated Li/Cl phosphinidenoid complex 2a (300 mg, 0.49 mmol), 12-crown-4 (95 \(\mu\)L, 0.48 mmol), \(^1^B\)BuLi (1.7 M in n-hexane, 0.34 mL) in 7 mL of THF was added benzaldehyde (70 \(\mu\)L, 0.58 mmol) at −78 °C leading to formation of a white precipitate. The reaction mixture was warmed to −15 °C in a cooling bath (ca. 2 h), and volatiles were evaporated in vacuo. The product was extracted with n-pentane (40 mL), and filtered. After evaporation of the solvent in vacuo, washed with n-pentane (3 × 1 mL) at −50 °C, dried, and thus obtained as a white solid.

Yield: 234 mg (0.38 mmol, 78%). \(^1^H\) NMR (CDCl\(_3\)) \(\delta = 3.6\) (d, 1H, \(J_{HP} = 5.6\) Hz, HP), 7.0-7.2 (m, 15H, CPh), 7.4-7.6 (m, 5H, Ph), \(^1^3^C\) (H)NMR (CDCl\(_3\)): \(\delta = 51.2\) (d, \(J_{CP} = 20.2\) Hz, PCO), 66.2 (d, \(J_{CP} = 13.7\) Hz, PCPh\(_3\)), 127.2 (d, \(J_{CP} = 3.3\) Hz, Ph), 128.4 (d, \(J_{CP} = 2.6\) Hz, Ph), 129.0 (d, \(J_{CP} = 1.7\) Hz, Ph), 129.1 (s, Ph), 139.2 (d, \(J_{CP} = 11.7\) Hz, Ph), 139.6 (d, \(J_{CP} = 6.3\) Hz, Ph), 202.3 (d, \(J_{CP} = 126.3\) Hz, cis-CO), 208. (d, \(J_{CP} = 49\) Hz, trans-CO).

Synthesis of complexes [M(CO\(_3\))\(_2\)[(Ph\(_3\)C)CHP(C,H\(_2\)O)\(_2\)]] (4d-f) and formation of 5d-f.

To freshly generated Li/Cl phosphinidenoid complexes 2a-c (a: 300 mg, 0.48 mmol; b: 300mg, 0.49 mmol, c: 300mg, 0.43mmol), 12-crown-4 (a: 95 \(\mu\)L, 0.48 mmol, b: 97 \(\mu\)L, 0.49 mmol, c: 69 \(\mu\)L, 0.43 mmol), \(^1^B\)BuLi (1.7 M in n-hexane, 0.34 mL), 1-3 | 5

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Formation of complexes 5d-f.

Complexes 5d-f are formed together with 4d-f under the same conditions with the following ratios: 4d:5d 5:1, 4e:5e 5:3 and 4f:5f 5:1. All attempts to separate 5d-f from 4d-f failed, but we succeeded to get a few crystals of 5e via crystallisation in diethyl ether at -30 °C so that the constitution was unambiguously confirmed. Besides, the methine CH resonance of HCPH3 was detected in the 1H NMR spectra of most fractions.

5d: \[^{31}\text{P}(^1\text{H})\text{NMR(THF)}\]: \(\delta_{P1} = 210.5, \delta_{P2,P3} = 3.8 \text{ Hz; } \delta_{P2} = 165.6, \delta_{P3} = 3.8 \text{ Hz.}\)

5e: \[^{1}\text{H}\text{NMR (THF-d8)}\]: \(\delta = 1.81 \text{ (br, 1H, CH), } 3.62 \text{ (br, 2H, CH), } 5.64 \text{ (s, 1H, HCPH3), } 6.64 \text{ (m, 1H, CH-} ^{sp2}\text{), } 7.14 \text{ (m, 1H, CH-} ^{sp3}\text{), } 7.22 – 7.24 \text{ (m, 4H, Ph-H), } 7.27 – 7.32 \text{ (m, 6H, Ph-H), } 7.42 – 7.47 \text{ (m, 4H, Ph-H), } 7.53 – 7.58 \text{ (m, 6H, HCPH3) } 7.63 – 7.68 \text{ (m, 3H, HCPH3), } 7.84 – 7.89 \text{ (m, 6H, HCPH3), } 190.3 \text{ ppm.}\)

Computational Details

DFT calculations were performed with the ORCA program. All geometry optimizations were run in redundant internal coordinates with tight convergence criteria, in the gas-phase using the B3LYP functional\(^ {21}\) together with the def2-TZVP basis set\(^ {22}\) in case of model complexes (P-methyl substituted), level A, or the smaller def2-SVP basis set\(^ {23}\) for P-trityl substituted complexes), level B. For Mo and W atoms the [SD(28,MWB)] or [SD(60,MWB)] effective core potentials (ECP) were used.\(^ {24}\) The latest Grimme’s semipirical atom-pairwise London dispersion correction (DFT-D3) was included in all calculations.\(^ {25}\) Solvent effects (THF) were taken into account via the COSMO solvation model.\(^ {26}\) Harmonic frequency calculations verified the nature of ground states or transition states (TS) having all positive frequencies or only one imaginary frequency, respectively. From these optimized geometries all reported data were obtained by means of single-point (SP) calculations using the more polarized def2-TZVPP\(^ {27}\) basis set. Reported energies were corrected for the zero-point vibrational term at the optimization level and obtained by means of the recently developed near linear scaling domain-based local pair natural orbital (DLPNO) method\(^ {28}\) to achieve coupled cluster theory with single-double and perturbative triple excitations (CCSD(T)), level A, or the spin component-scaled Møller-Plesset 2 (SCS-MP2) method,\(^ {29}\) level B. For the sake of comparison, in case of all model systems, energy values were also computed with other high level single reference method, such as CEPA (Coupled Electron-Pair Approximation),\(^ {30}\) here the slightly modified NCEPA1 version implemented in ORCA was used,\(^ {31}\) with the aid of local pair natural orbital (LPNO) schemes;\(^ {32}\) the SCS-MP2 theory and
the double-hybrid-meta-GGA functional PWP85\(^{13}\) together with the D3 correction were also used. For a set of twenty values with model systems (see Table S 1), the LPNO-NCEPA1 method performed very accurately according to the small RMSD (root mean square deviation) displayed (0.32 kcal/mol) in relation to DLPNO-CCSD(T); among the less computationally demanding methods, therefore accessible for bigger molecular systems as the real P-trityl substituted derivatives, SCS-MP2 clearly outperformed (RMSD = 0.36 kcal/mol) PWP85-D3 (RMSD = 0.79 kcal/mol) and hence was selected as "level B".

Conclusions

We have demonstrated that reactions of P-trityl substituted Li/Cl phosphinidenoid complexes with carbonyl derivatives are very sensitive towards steric crowding. In case of benzaldehyde, oxaphosphirane complexes were obtained, whereas exclusively complexes bearing P-ligands with fused ring systems were observed in case of benzophenone. DFT studies show that complexes with the bicyclic P-ligand could be formed from a short-lived oxaphosphirane complex intermediate via P-C ring cleavage, followed by P-C(phenyl) cyclization and either pericyclic or (most likely) water catalyzed (concerted or stepwise) suprafacial [1,3]H shift. The novel pentacyclic P-ligand in the other product arises from a phospha-Diels-Alder reaction between two reactive intermediates, one of which being a 2-phosphafurane complex formed via a phospha-ene elimination of HCPH\(_3\).

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Notes and references

‡ This work is dedicated to the memory of Prof. Reinhard Schmutzler.
‡‡ Electronic Supplementary Information (ESI) available: X-ray analysis of 3a-b, 4f and 5e; comparison of energetics at various computational levels; structures (Cartesian coordinates) and energies for all computed species. See DOI: 10.1039/c000000x/

An alternative lower barrier route (not studied computationally) would involve initial deprotonation of both \(8h\) and \(8h'\), followed by regio- and stereoselective kinetically controlled reprotonation at the most accessible side (opposite to the bulkier trityl group in real systems) of the resulting extensively delocalized benzyl-type cation, leading to complex \(4h\) (diastereomer \(4h'\) is 0.70 kcal/mol more stable).
15. COSMO\(_{\text{thd}}\)/DLPNO-CCSD(T)/def2-TZVPPecp for \(3h\rightarrow8h,8h'\); COSMO\(_{\text{thd}}\)/SCS-MP2/def2-TZVPcempc for \(8e\rightarrow10e\rightarrow12\).
17. For comparative purposes the relative energies of the hydrated adducts of \(8h\) and \(4h\) were set to the same value of the respective anhydrous species, therefore neglecting the small hydration energies.
Mo [SD(28, MWB)] and W [SD(60, MWB)] have been obtained from Turbomole basis set library at ftp://ftp.chemie.uni-karlsruhe.de/pub/basen/. ECP basis sets for Mo [def2-SVP] and W [def2-TZVP]: F. Weigend, R. Ahlrichs, Phys.Chem.Chem.Phys., 2005, 7, 3297-3305.


CPh₃ as a functional group in P-heterocyclic chemistry: elimination of HCPH₃ in the reaction of P-CPh₃ substituted Li/Cl phosphinidenoid complexes with Ph₂C=O

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Reaction of Li/Cl phosphinidenoid complexes 2 (M = Cr, Mo, W) react differently with benzaldehyde or benzophenone. The latter resulted in the formation of complexes 4 and 5, the former bearing a benzo[c]-1,2-oxaphospholane and the latter a novel pentacyclic P-ligand thus also revealing elimination of HCPH₃.

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Electronic Supplementary Information (ESI) available: X-ray analysis of 3a,b, 4f and 5e; computational details; comparison of energetics at various computational levels; structures (Cartesian coordinates) and energies for all computed species. See DOI: 10.1039/c0000000/