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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

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CPh_3 as a functional group in P-heterocyclic chemistry: elimination of $HCPh_3$ in the reaction of P-CPh_3 substituted Li/Cl phosphinidenoid complexes with Ph_2C=O

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C. Murcia García,[a] A. Espinosa Ferao,*[b] G. Schnakenburg[a] and R. Streubel,*[a]

P-CPh_3 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 benzofused 2-phosphafurane complex **8**, one of the fragmentsundergoing water-catalyzed [1,3]H shift (**4**) and the other (**11**) formed via elimination of $HCPh_3$.

Introduction

The ability to stabilize a negative or positive charge, or a radical centre makes the triphenylmethyl group (CPh_3 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 derivatives[3], 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 phosphaalkyne.[6] In a preliminary study Schmutzler showed that trityl can serve as a leaving group if such phosphane derivatives are treated with very strong acids.[7]

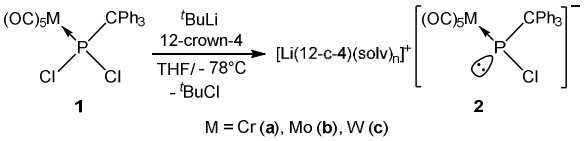
On the other hand, we recently demonstrated that the accessibility of transition-metal oxaphosphirane complexes was hugely facilitated due to the availability of Li/Cl phosphinidenoid complexes.[8] Of particular importance was the first derivative bearing the sterically demanding trityl group at phosphorus,[8d] 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 CPh_3 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/Cl 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**, initially developed for **1c**/**2c**.[8d]

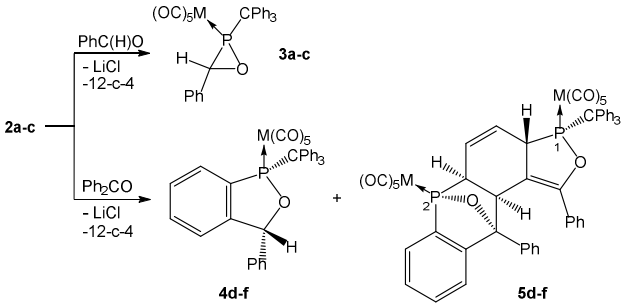


Scheme 1. Synthesis of *P*-CPh_3 phosphinidenoid complexes **2a-c**.

Reaction of Li/Cl phosphinidenoid complexes **2a,b,c**[8d] with benzaldehyde led to the clean formation of oxaphosphirane derivatives **3a,b,c**[8d] (Scheme 2) which were fully characterized

[a] Institut für Anorganische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Str. 1, D-53121 Bonn, Germany. Fax: (49)228-739616; Tel: (49)228-735345; e-mail: r.streubel@uni-bonn.de.
[b] Departamento de Química Orgánica, Facultad de Química, Universidad de Murcia, Campus de Espinardo, E-30071 Murcia, Spain. Fax: (34)868-884149; Tel: (34)868-887489; e-mail: artuesp@um.es.
† 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/c000000x/

by means of NMR, mass spectrometry as well as X-ray analysis (see ESI for **3a,b**).



Scheme 2. Synthesis of *P*-CPh_3 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*-CPh_3 group, compounds **2a-c** were reacted with benzophenone. To our great surprise, the $^{31}P\{^1H\}$ 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 $^{31}P\{^1H\}$ NMR monitoring of the reactions were performed (-78 to 25 °C), but oxaphosphirane complexes could not be detected. The $^{31}P\{^1H\}$ 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 $^5J_{P,P}$ 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. $^{31}P\{^1H\}$NMR data (δ [ppm], and $J_{P,P}$ [Hz]) of **3a-c**, **4d-f**, **5d-f** and **4**:**5** ratios in THF solution.

Metal	3a-c	4d-f	5d-f (P^1/P^2)	$^5J_{P1,P2}$	Ratio 4:5
Cr	58.7	190.3	210.5/165.6	3.8	5:1
Mo	33.4	167.4	186.3/138.2	3.8	5:3
W	16.0[8d]	145.1	164.4/112.3	3.8	5:1

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 diethylether at -30 °C. The X-ray structure of the pentacyclic complex **5e** (Figure 2) surprisingly showed (formally) two units of Ph_2CO, 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 $HCPh_3$ 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).

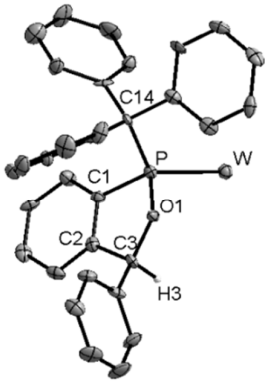


Figure 1. Crystal structure of complex **4f** (thermal ellipsoids are shown with 50% probability level); all hydrogen atoms (except H3), as well as carbonyl groups at the metal are omitted for clarity; selected bond lengths (Å) and angles (°): P-W 2.5101(3), P-C14 2.9161(2), P-O 1.6423(2), C1-C2 1.4083(2), P-O1-C3 112.748(8), P1-C1-C2 107.616(9), C1-C2-C3 113.966(8), C2-C3-O1104.406(8).

Quantum chemical calculations were used to study the formation of products **4** and **5** in the reaction of trityl substituted phosphinidenoids **2** with benzophenone. For the sake of computational efficiency the first part of the mechanistic search was performed starting from *P*-Me model complexes **3g,h** (Scheme 3) at the highest computational level (level A, see below).

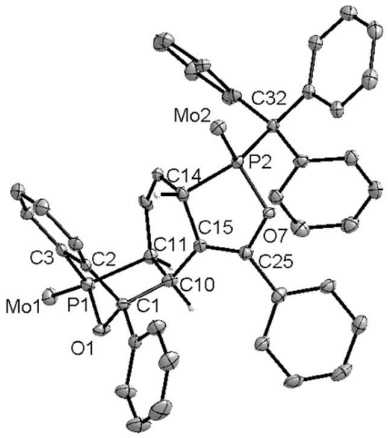
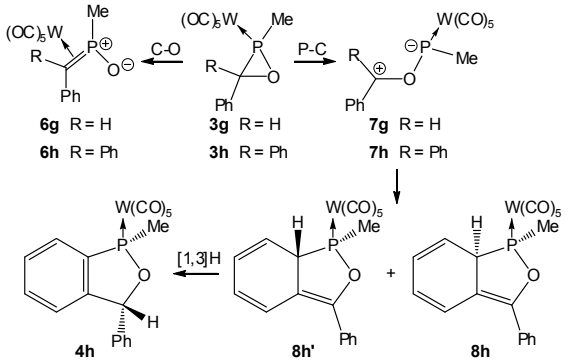


Figure 2. Crystal structure of complex **5e** (thermal ellipsoids are shown with 50% probability level); all hydrogen atoms (except H10A, H11A and H14A), and carbonyl groups at the metals are omitted for clarity; selected bond lengths (Å) and angles (°): P1-Mo1 2.4258(1), P1-O1 1.6456, C2-C3 1.3922(6), P2-Mo2 2.5259(2), P2-C32 1.9597(7), C15-C25 1.3667(5), C14-C15 1.5256(6), C10-C11 1.5457(6), P1-O1-C1 102.597(3), O1-C1-C10 100.224(4), C1-C10-C11 105.523(3), C10-C11-P1 102.424(3), P2-O7-C25 113.674(5), O7-C25-C15 116.226(4), C25-C15-C14 113.486(3), C15-C14-P2 102.959(1).



Scheme 3. Mechanistic proposal for the formation of **4h.**

Tungsten complexes were used as models to enable comparison with previous reports[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 **3g** preferentially undergoes exergonic (-6.57 kcal/mol) C-O bond cleavage with a moderate energy barrier 28.91 kcal/mol), leading to a *side-on* phosphaalkene *P*-oxide complex **6g**. In contrast, a higher barrier P-C bond cleavage path (37.72 kcal/mol) being rather endergonic (+28.90 kcal/mol) affords **7g**. In case of the diphenyl model system **3h**, both processes have a lower barrier (Figure 3), the P-C bond cleavage product **7h** being comparatively stabilized with respect to **7g** due to extensive delocalization of the positive charge. In stark contrast, the C-O cleavage product **6h** is destabilized presumably due to steric reasons.

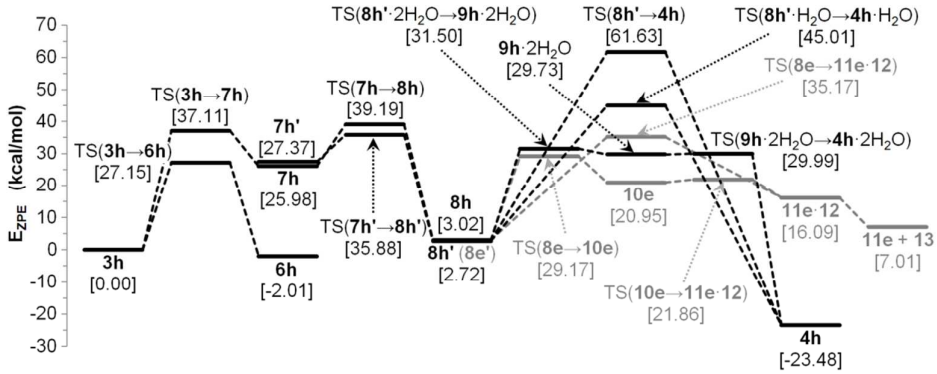
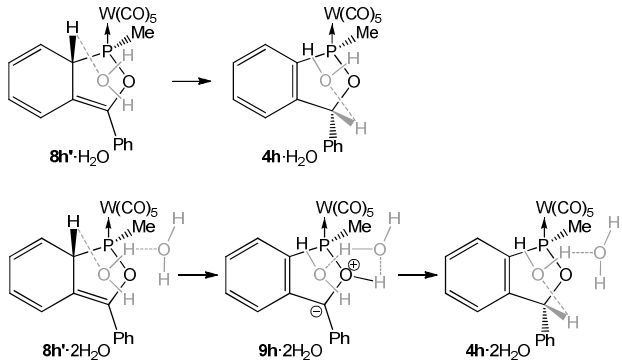


Figure 3: Computed[15] ZPE-corrected energy profile for the conversion of complexes **3** into **4** and **11**. In grey the relative energies for full trityl substituted complexes (relative energy of **8e'** is set to the same value than **8h'**).

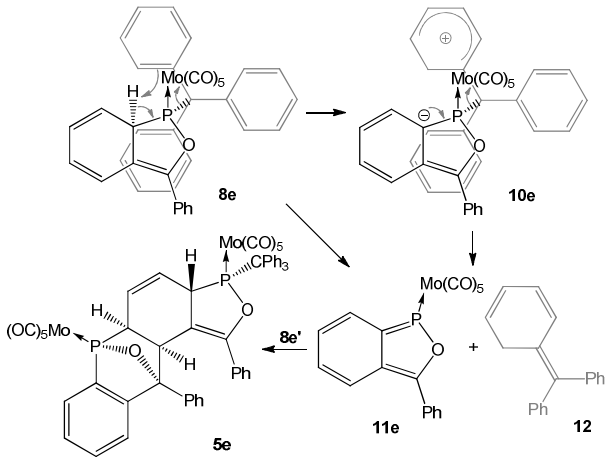
Therefore, the C-O bond cleavage equilibrium for **3h** is expected to be shifted to the rather reactive (more slowly formed) P-C bond cleavage product **7h** which readily undergoes cyclization by attack of the nucleophilic P atom at the closest phenyl *ortho* position, thus giving rise to bicyclic derivative **8h**. Complex **7h** exists as two conformers, differing in the helical orientation of the Ph_2C^+ moiety, the most unstable of which (**7h'**) cyclizes to the most stable diastereomer of the bicyclic complex **8h'**, whereas the other helical isomer **7h** gives rise to less stable diastereomer **8h**. Worth mentioning is that oxaphosphirane complex **3** might not be formed in real systems due to steric congestion and, alternatively, ylide complex **7** could directly result upon reaction of phosphinidenoid complex **2** with benzophenone and evolve towards the five-membered derivative **8**.

Formation of the final (model) complex **4h**, whose comparative stability arises from the gain of aromatic character in the benzo-fused ring, could be explained through *supra* [1,3]H shift to the benzylic position in diastereomer **8h'**. According to Woodward-Hoffmann orbital symmetry rules[13] this process is thermally forbidden and displays a high energy barrier.[14] In order to explain the formation of **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 **8h'→4h** rearrangement. A water molecule has been used as model for such a catalytic species (*vide infra*),[16] although any other proton carrier species present in the reaction medium could similarly account for the catalyzed proton transfer. Thus **8h'**·H_2O was found to isomerize to **4h**·H_2O (Scheme 4) through a much lower yet significantly high pericyclic transition state ($\Delta\Delta E_{ZPE}$ = 42.30 kcal/mol) (Figure 3)[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 ($\Delta\Delta E_{ZPE}$ = 28.79 kcal/mol) which leads to a dihydrated zwitterion **9h**·$2H_2O$ (Scheme 4), whose almost barrierless (water-mediated) O-to-C [1,2]H shift affords the final model product **4h**·$2H_2O$.



Scheme 4. Mechanistic proposals for the water-catalyzed isomerization of **8h'** into **4h.**

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 diphenylmethylidenecyclohexadiene **12** as by-product (Scheme 5). The latter can then isomerize to the more stable triphenylmethane **13** (ΔE_{ZPE} = -26.58 or -27.20 kcal/mol at A or B levels, respectively). The above **12**→**13** transformation is again thermally forbidden as a concerted (pericyclic) process, but could alternatively take place in a water-catalyzed manner (not studied), as the previously described **8h'**·nH_2O→**4h**·nH_2O transformation, or when coupled to the **8h'**→**4h** rearrangement, therefore **12** acting as the required simultaneous HB donor and acceptor species (*vide supra*), although in a non-catalytic fashion.



Scheme 5. Proposal for the formation of **5**.

The alternative two-step proton transfer through zwitterionic complex **10e** followed by P-group detachment constitutes a lower energy sequence to **11e**. The resulting non-aromatic (*i.e.* reactive) bicyclic 2-phosphafurane complex intermediate[18] **11e** features a cyclic, conformationally *s-cis* locked phosphadiene character and, therefore, can be expected to behave as 4π-component and undergo a phospha-Diels-Alder[19] reaction. The 2π 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 (^{1}H: 300.1 MHz, ^{13}C: 75.0 MHz and ^{31}P: 121.5 MHz,) using $CDCl_3$ as solvent; shifts are given in ppm relative to external tetramethylsilane (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P).

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 P_2O_5. 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)$_5$Cr{Ph$_3$CPCl}] (2a) for the spectroscopic characterization (2a)

250 mg (0.47 mmol) of [(Ph_3CPCl_2)Cr(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 ^{t}BuLi [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*) δ = 3.74 (s, 16H, 12-c-4), 6.9-7.5 (m, 15H, CPh_3). $^{13}C\{^{1}H\}$NMR (THF-*d*8)66.9 (d, $^{1}J_{C,P}$ = 22.8 Hz, CP), 68.3 (s, 12-c-4), 125.1 (s, *para*-Ph), 125.5 (d, $^{5}J_{C,P}$ = 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, $^{3}J_{C,P}$ = 15.7 Hz, *ortho*-Ph), 131.1 (s, *ortho*-Ph), 131.7 (d, $^{3}J_{C,P}$ = 5.7 Hz, *ortho*-Ph), 220.6 (d, $^{2}J_{C,P}$= 6.9 Hz, *cis*-CO), 221.6 (d, $^{2}J_{C,P}$= 20.1 Hz, *trans*-CO). $^{31}P\{^{1}H\}$NMR (THF-*d8*) 310.42 ppm; this signal displayed a shoulder on the high-field side (ratio ca. 3:1) that corresponds to the ^{37}Cl isotopomer of **2a**.

Synthesis [Li(12-crown-4)(THF)][(OC)$_5$Mo{Ph$_3$CPCl}] (2b) for the spectroscopic characterization

250 mg (0.37 mmol) of [(Ph_3CPCl_2)Mo(CO)$_5$] were dissolved in THF-*d8* (5 mL) and 70 µL (1eq.) of 12-crown-4 were added. The solution was then cooled to -80 ◦C and 1.2 eq. of ^{t}BuLi [1.7 M in *n*-pentane] were given dropwise and the solution was stirred 5 minutes. After that, the solution was transferred into a cooled (-90°C) NMR tube via double needle and was measured first at -80°C and the phosphinidenoid complex was then further characterized at -60°C.

2b: Deep red solution. ^{1}H NMR (THF-*d8*, -60°C) δ = 3.79 (s, 16H, 12-c-4), 7.0-7.66 (m, 15H, CPh_3). $^{13}C\{^{1}H\}$NMR (THF-*d*8, -60°C): 66.3 (s, 12-c-4), 67.1 (d, $^{1}J_{C,P}$ = 22.1 Hz, CP), 123.5 (s, *para*-Ph), 123.7 (s, *para*-Ph), 124.7 (d, $^{5}J_{C,P}$ = 1.35 Hz, *para*-Ph), 125.5 (s, *meta*-Ph), 125.9 (s, *meta*-Ph), 126.8 (s, *meta*-Ph), 128.2 (d, $^{3}J_{C,P}$ = 17.8 Hz, *ortho*-Ph), 130.4 (s, *ortho*-Ph), 130.9 (d, $^{3}J_{C,P}$ = 9.7 Hz, *ortho*-Ph), 147.2 (d, $^{2}J_{C,P}$ = 22.6 Hz, *ipso*-Ph), 148.9 (s, *ipso*-Ph), 149.2 (d, $^{2}J_{C,P}$= 9.0 Hz, *ipso*-Ph), 208.8 (d, $^{2}J_{C,P}$= 8.0 Hz, *cis*-CO), 216.2 (d, $^{2}J_{C,P}$= 24 Hz, *trans*-CO). $^{31}P\{^{1}H\}$NMR (THF-*d8*, -60°C): 280.43 ppm (major); this signal displayed a shoulder on the high-field side (ratio ca. 3:1) that corresponds to the ^{37}Cl isotopomer of **2b**.

Synthesis of [(OC)$_5$Cr{Ph$_3$CPOC(H)Ph}] (3a)

To a freshly generated Li/Cl phosphinidenoid complex **2a** (300 mg, 0.48 mmol), 12-crown-4 (95 µL, 0.48 mmol), tBuLi (1.7 M in *n*-hexane, 0.34 mL) in 7 mL of THF) was added benzaldehyde (70 µL, 0.58 mmol) at −78 °C leading tofor-mation of a white precipitate. The reaction mixture was warmed up to −15 °C in a cooling bath (ca. 2 h), and volatiles were evaporated in vacuum. The product was extracted with *n*-pentane (40 mL), and filtered. After evaporation of the sol-vent *in vacuo*, washed with *n*-pentane (3 × 1 mL) at −50 °C, dried, and thus obtained as white solid with a slight greenish touch; the origin of the color is not clear.

3a: Yield: 264 mg (0.46 mmol, 88%). ^{1}H NMR ($CDCl_3$) δ = 3.9 (d, 1H, $^{2}J_{H,P}$ = 2.2 Hz, CHP), 7.0-7.2 (m, 15H, CPh_3), 7.4-7.6 (m, 5H, Ph). $^{13}C\{^{1}H\}$NMR ($CDCl_3$): δ = 59.1 (d, $^{1}J_{C,P}$ = 20.6 Hz, PCO), 67.5 (d, $^{1}J_{C,P}$ = 14.1 Hz, $PCPh_3$), 125.4 (d, $J_{C,P}$ = 3.3 Hz, Ph), 127.7 (d, $J_{C,P}$ = 2.6 Hz, Ph), 129.1 (d, $J_{C,P}$ = 1.7 Hz, Ph), 129.7 (s, Ph), 133.2 (d, $J_{C,P}$ = 11 Hz, Ph), 138.5 (d, $^{2}J_{C,P}$ = 6.3 Hz, *ipso*-Ph), 211.6 (d, $^{2}J_{C,P}$ = 14.5 Hz, *cis*-CO), 214.3 (d, $^{2}J_{C,P}$ = 37 Hz, *trans*-CO).$^{31}P\{^{1}H\}$ ($CDCl_3$) δ = 58.7. IR (neat): ṽ [cm^{-1}] = 2069, 1996, 1959, (s, CO). MS:selected data *m/z* (%) 572.0 $[M]^+$, 432.1 (30) $[M\text{-}5CO]^+$, 326.0 (15) $[M–5CO\text{-}C_7H_6O]^+$, 243.1 (100) $[CPh_3]^+$.Elemental analysis (%) calculated for $C_{31}H_{21}CrO_6P$ (%) C: 65.04, H: 3.70; found: C: 65.93, H: 3.85.

Synthesis of [(OC)$_5$Mo{Ph$_3$CPOC(H)Ph}] (3b)

To a freshly generatedLi/Cl phosphinidenoid complex **2a** (300 mg, 0.49 mmol), 12-crown-4 (95 µL, 0.48 mmol), ^{t}BuLi (1.7 M in *n*-hexane, 0.34 mL) in 7 mL of THF) was added benzaldehyde (70 µL, 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.

3b: Yield: 234 mg (0.38 mmol, 78%). ^{1}H NMR ($CDCl_3$) δ = 3.6 (d, 1H, $^{2}J_{H,P}$= 5.6 Hz, HP), 7.0-7.2 (m, 15H, CPh_3), 7.4-7.6 (m, 5H, Ph). $^{13}C\{^{1}H\}$NMR ($CDCl_3$): δ = 51.2 (d, $^{1}J_{C,P}$ = 20.2 Hz, PCO), 66.2 (d, $^{1}J_{C,P}$ = 13.7 Hz, $PCPh_3$), 127.2 (d, $J_{C,P}$ = 3.3 Hz, Ph), 128.4 (d, $J_{C,P}$ = 2.6 Hz, Ph), 129.0 (d, $J_{C,P}$ = 1.7 Hz, Ph), 129.1 (s, Ph), 139.2 (d, $J_{C,P}$ = 11 Hz, Ph), 139.6 (d, $^{2}J_{C,P}$ = 6.3 Hz, Ph), 202.3 = 126.3 Hz, *cis*-CO), 208 (d, $^{2}J_{C,P}$ = 49 Hz, *trans*-CO).$^{31}P\{^{1}H\}$($CDCl_3$) δ = 33.4 ppm. IR (neat): ṽ [cm^{-1}] = 2077, 1996, 1968 (s, CO). MS: selected data *m/z* (%) 618.0 $[M]^+$, 478.0 (20) $[M\text{-}5CO]^+$, 372 (5) $[M–5CO\text{-}C_7H_6O]^+$, 243.1 (100) $[CPh_3]^+$.Elemental analysis (%) calculated for $C_{31}H_{21}MoO_6P$ (%) C: 60.70, H: 3.43; found: C: 61.11, H: 3.65.

Synthesis of complexes [M(CO)$_5${(Ph$_3$C)CHP(C$_5$H$_5$)$_2$-O}] (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 µL, 0.48 mmol, **b**: 97 µL, 0.49 mmol, **c**: 69 µL, 0.43 mmol), ^{t}BuLi (1.7 M in *n*-hexane, **a**: 0.34 mL, **b**: 0.36 mL, **c**: 0.25 mL) in 7 mL of THF were added benzophenone (0.69 M in THF, **a**: 1.4 mL, **b**: 1.4 mL, **c**: 0.62 mL) at −78 °C leading to the formation of a white precipitate. Thereaction mixture was warmed to ambient temperature (4h of stirring) until complete consumption of the corresponding phosphinidenoid complex and volatiles were evaporated in *vacuo*. The product **4d** could not be obtained in pure form due to decomposition during purification, and**4e**could be identified only from the reaction mixture.**4f** 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 white solid.

4d: ^{1}HNMR (THF-*d8*): δ =5.64 (s, 1H, HCPh$_3$). 6.27 (s br, 1H, POC(H)Ph), 6.51 (d, 1H, $^{3}J_{H,H}$ = 8.11 Hz, Ar-H), 7.08 (d, 1H,$^{3}J_{H,H}$ = 7.40 Hz, CPh_3-H), 7.15 (d, 2H, $^{3}J_{H,H}$ = 6.70 Hz, Ar-H), 7,22 – 7,39

(m, 3H, Ph-H, CPh_3-H), 7,47 – 7,56 (m, 6H, CPh_3-H), 7,63 – 7,73 (m, 3H, CPh_3 - H, Ph-H), 7,81 – 7,83 (m, 3H, Ph-H, CPh_3-H), 7.84 – 7.89 (m, 2H, Ar-H).$^{13}C\{^1H\}$ NMR (THF-*d8*): δ = 69.5 (d, $^{2/3}J_{P,C}$= 2.5 Hz, POC(H)Ph), 86.3 (d, $^1J_{P,C}$ = 8.9 Hz, Ph_3C), 125.5 (s, C-Ph), 125.7 (d, $J_{P,C}$ = 10.5 Hz, Ar-C), 126.1 (s, *para*-Ph), 126.3 (d, JP,C = 10.5 Hz, *ortho*-Ph), 127.6 (s, *meta*-Ph), 127.7 (s, *para*-Ph), 128.0 (d, $^1J_{P,C}$= 14.2 Hz, C-Ph), 128.8 (s, *ortho*-Ph), 129.2 (s, *meta*-Ph), 131.5 (s, *ortho*-Ph), 137.4 (s, C-Ph), 139.3 (d, $J_{P,C}$ = 22.9 Hz, *ipso*-Ph), 142.7 – 143.2 (m, Ph-C), 143.7 (s, *ipso*-Ph), 143.9 (s, *ipso*-Ph), 146,9 (s, Ph-C), 199.2 (dsat, $^2J_{P,C}$ = 9.6 Hz, $^1J_{W,C}$ = 132.0 Hz, *cis*-CO), 204.3 (d, $^2J_{P,C}$ = 32.9 Hz, *trans*-CO).$^{31}P\{^1H\}$ (THF)δ = 190.3 ppm.

4e: ^{1}HNMR (THF-*d8*): δ =5.64 (s, 1H, $\underline{H}CPh_3$); 6.35 (s br, 1H, POC(H)Ph), 6.58 (d, 1H, $^3J_{H,H}$ = 8.11 Hz, Ar-H), 7.23 (d, 1H, $^3J_{H,H}$ = 7.80 Hz, CPh_3-H), 7.18 (d, 2H, $^3J_{H,H}$ = 6.52 Hz, Ar-H), 7,22 – 7,45 (m, 3H, Ph-H, CPh_3-H), 7,47 – 7,56 (m, 6H, CPh_3-H), 7,68 – 7,83 (m, 3H, CPh_3 - H, Ph-H), 7,81 – 7,83 (m, 3H, Ph-H, CPh_3-H), 7.84 – 7.89 (m, 2H, Ar-H).$^{13}C\{^1H\}$ NMR (THF-*d8*): δ = 70.1 (d, $^{2/3}J_{P,C}$= 2.1 Hz, POC(H)Ph), 86.3 (d, $^1J_{P,C}$ = 8.5 Hz, Ph_3C), 123.1 (s, C-Ph), 123.7 (d, $J_{P,C}$ = 8.5 Hz, Ar-C), 125.3 (s, *para*-Ph), 125.8 (d, $J_{P,C}$ = 10.5 Hz, *ortho*-Ph), 126.2 (s, *meta*-Ph), 126.7 (s, para-Ph), 128.2 (d, $^1J_{P,C}$= 12.2 Hz, C-Ph), 128.8 (s, *ortho*-Ph), 129.7 (s, *meta*-Ph), 131.5 (s, *ortho*-Ph), 136.0 (s, C-Ph), 138.8 (d, $J_{P,C}$ = 20.2 Hz, *ipso*-Ph), 140.1 – 142.6 (m, Ph-C), 143.2 (s, *ipso*-Ph), 143.8 (s, *ipso*-Ph), 145.1 (s, Ph-C), 19.8 (dsat, $^2J_{P,C}$ = 6.6 Hz, $^1J_{W,C}$ = 132.0 Hz, *cis*-CO), 202.3 (d, $^2J_{P,C}$ = 32.9 Hz, *trans*-CO).$^{31}P\{^1H\}$ NMR (THF-*d8*) δ = 167.4. Elemental analysis is not shown because **4d** and **5d** could not be separated (ratio 5:1), but the NMR resonances of **4d** could be assigned.

4f: Yield: 204 mg (0.26 mmol, 68 %). ^{1}H NMR (THF-d8): δ =5.58 (s, 1H, $\underline{H}CPh_3$), 6.50 (s br, 1H, POC(H)Ph), 7.15 (d, 1H, $^3J_{H,H}$= 6.70 Hz, Ar-H), 6.67 (d, 2H, $^3J_{H,H}$ = 8.18 Hz, Trt-H), 7.02 (t, 1H, $^3J_{H,H}$ = 8.80 Hz, Ar-H), 7,10 – 7,37 (m, 6H, Ph-H, Trt-H), 7,43 – 7,62 (m, 6H, Trt-H), 7,63 – 7,73 (m, 3H, TrtH, Ph-H), 7,77 – 7,85 (m, 3H, Ph-H, Trt-H), 7.91 (d, 2H, $^3J_{H,H}$ = 6.93 Hz, Ar-H).$^{13}C\{^1H\}$ NMR (THF-d8):δ = 68.6 (d, $^{2/3}J_{P,C}$= 2.1 Hz, POC(H)Ph), 86.3 (d, $^1J_{P,C}$= 8.7 Hz, Ph_3C), 123.0 (d, $J_{P,C}$ = 7.4 Hz, Ar-C), 126.3 (s, *para*-Ph), 126.5 (d, $J_{P,C}$ = 10.0 Hz, *ortho*-Ph), 127.3 (s, *meta*-Ph), 128,2 (s, *para*-Ph), 129,5 (s, *ortho*-Ph), 130,0 (s, *meta*-Ph), 132,4 (s, *ortho*-Ph), 137,6 (s, C-Ph), 139,2 – 140.0 (m, Ph-C), 141,1 (d, $J_{P,C}$ = 22.9 Hz, *ipso*-Ph), 143,2 (d, $J_{P,C}$ = 11.6 Hz, *ipso*-Ph), 143.9 (s, *ipso*-Ph), 146,9 (s, Ph-C), 196.5 (dsat, $^2J_{P,C}$ = 7.1 Hz, $^1J_{W,C}$ = 134.0 Hz, cis-CO), 199,5 (d, $^2J_{P,C}$ = 30,9 Hz, *trans*-CO).$^{31}P\{^1H\}$ NMR (THF-*d8*) δ = 145.1, $^1J_{P,W}$ = 277.5 Hz.IR (neat): ṽ [cm^{-1}] = 2076, 1958, 1937, (s, CO).MS: selected data*m/z* (%) 780.1 $[M]^+$, 537.0 (3) $[M–CPh_3]^+$, 509.0 (1) $[M–CPh_3–CO]^+$, 425.1 (20) $[M–CPh_3–CO–3CO]^+$, 397.1 (40) $[M–CPh_3–CO–3CO–CO]^+$, 243.2 (100) $[CPh_3]^+$. Elemental analysis (%) calculated for $C_{37}H_{25}WO_6P$ (%) C: 56.94, H: 3.23; found: C: 57.28, H: 3.82.

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 diethylether at -30 °C so that the constitution was unambigously confirmed. Besides, the methine CH resonance of $HCPh_3$ was detected in the 1H NMR spectra of most fractions.

5d: $^{31}P\{^1H\}$ NMR(THF): δ_{P1} = 210.5, $^5J_{P1,P2}$ = 3.8 Hz; δ_{P2} = 165.6, $^5J_{P1,P2}$ = 3.8 Hz.

5e: ^{1}HNMR (THF-*d8*): δ = 1.81 (s br, 1H, CH), 3.62 (s br, 2H, CH),5.64 (s, 1H, $HCPh_3$),6.64 (m_c, 1H, CH-sp^2),7.14 (m_c, 1H, CH-sp^2), 7.22 – 7.24 (m, 4H, Ph-H),7.27 – 7.32 (m, 6H, Ph-H),7.42 – 7.47 (m, 4H, Ph-H), 7.53 – 7.58 (m, 6H, CPh_3-H), 7.63 – 7.68 (m, 3H, CPh_3-H), 7.84 – 7.89 (m, 6H, CPh_3 - H).$^{31}P\{^1H\}$ (THF): δ_{P1} = 186.3, $^5J_{P1,P2}$ = 3.8 Hz; δ_{P2} = 138.2 $^5J_{P1,P2}$ = 3.8 Hz.$^{13}C\{^1H\}$ NMR (THF-d8): δ = 56.4 (s br, POC(H)Ph), 86.7 (d, $^1J_{P,C}$= 9.0 Hz, Ph_3C), 125.6 (s, Ar-C), 126.7 (s, *para*-Ph), 127.6 (br. s, *ortho*-Ph), 128.9 (s, *meta*-Ph), 129.2 (s, *para*-Ph), 131.5 (s, *ortho*-Ph), 137.4 (s, *meta*-Ph), 143.7 (s, *ipso*-Ph), 204.2 (dsat, $^2J_{P,C}$ = 8.4 Hz, *cis*-CO), 221.4 (d, $^2J_{P,C}$ = 54,3 Hz, *trans*-CO) other signals could not be assigned. $^{31}P\{^1H\}$ NMR (THF): δ_{P1} = 186.3, $^5J_{P1,P2}$ = 3.8 Hz; δ_{P2} = 138.2, $^5J_{P1,P2}$ = 3.8 Hz.

5f: $^{31}P\{^1H\}$ NMR (THF): δ_{P1} = 164.4, $^5J_{P1,P2}$ = 3.8 Hz; δ_{P2} = 112.3, $^5J_{P1,P2}$ = 3.8 Hz.

Computational Details

DFT calculations were performed with the ORCA program.[20] All geometry optimizations were run in redundant internal coordinates with tight convergence criteria, in the gas-phase and 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 full (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 semiempirical 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 NCEPA/1 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 PWPB95[33] 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) PWPB95-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/

1 M. Gomberg, *J. Am. Chem. Soc.* 1900, **22**, 757.
2 V. Plack, J. R. Goerlich, A. Fischer, H. Thönnessen, P. G. Jones, R. Schmutzler, *Z. Anorg. Allg. Chem.* 1995, **621**, 1080.
3 V. Plack, J. R. Goerlich, R. Schmutzler, *Z. Anorg. Allg. Chem*., 1999, **625**, 919.
4 V. Plack, J. R. Goerlich, A. Fischer, R. Schmutzler, *Z. Anorg. Allg.Chem.,* 1999, **625**, 1979.
5 V. Plack, R. Schmutzler, *Phosphorus, Sulfur, Silicon Rel. Elem.,* 1999, **144–146**, 273.
6 J. G. Cordaro, D. Stein, H. Grützmacher, *J. Am. Chem. Soc.*, 2006, **128**, 14962.
7 V. Plack, J. R. Goerlich, R. Schmutzler, *Z. Anorg. Allg. Chem.*, 1998, **624**, 1940.
8 a) A. Özbolat, G. von Frantzius, M. Nieger and R. Streubel, *Angew. Chem. Int. Ed.,* 2007, **46**, 9327, b) M. Bode, G. Schnakenburg, P.G. Jones, R. Streubel, *Organometallics,* 2008, **27**, 2664-2667, c) R. Streubel, A. Özbolat-Schön, G. Von Frantzius, H. Lee, G. Schnackenburg, D. Gudat, *Inorg. Chem*., 2013, **52(6)**, 3313-3325. d) V. Nesterov, G. Schnakenburg, A. Espinosa, R. Streubel, *Inorg. Chem.* 2012, **51**, 12343-12349.
9 A. Espinosa, R. Streubel, *Chem.—Eur. J.*, 2012, **18**, 13405; here DFT studies on SET-induced homolytic exo P-C bond cleavage of *P*-trityl substituted oxaphosphirane complexes are described.
10 V. Plack, J. R. Goerlich, A. Fischer, H. Thönnessen, P. G. Jones, R. Schmutzler, *J. Fluor. Chem.*, 2000, **101**, 125.
11 V. Nesterov, A. Espinosa, G. Schnakenburg, R. Streubel, Chem. Eur. J., 2014, **20**, 7010-7016.
12 a) R. Streubel, C. Murcia-García, G. Schnakenburg, A. Espinosa Ferao, Organometallics, 2015, **34**, 2676. b) M. Klein, G. Schnakenburg, A. Espinosa Ferao, R. Streubel, *Dalton Trans.*, **2015**, DOI: 10.1039/C5DT03404C.
13 a) R. B. Woodward, R. Hoffmann:The Conservation of Orbital Symmetry, Verlag Chemie, Weinheim, 1–178, 1970. b) I. Frank, J. Friedrichs, Nat. Chem., 2009, **1**, 264-265. c) S. Sharma, T. Rajale, D. K. Unruh, D. Birney, J. Org. Chem., 2015, DOI: 10.1021/acs.joc.5b01355.
14 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 $COSMO_{THF}$/DLPNO-CCSD(T)/def2-TZVPPecp for **3h→8h,h'**; $COSMO_{THF}$/SCS-MP2/def2-TZVPPecp for **8e'→10e+12**.
16 a) C. J. Wu, L. E. Fried, L. H. Yang, N. Goldman, S. Bastea, *Nature Chem.*, 2009, **1**, 57-62. b) Z. Zhang, Y. Du, N. G. Petrik, G. A. Kimmel, I. Lyubinetsky, Z. Dohnálek, *J. Phys. Chem. C*, 2009, **113**, 1908-1916.
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.
18 V. Mouries, F. Mercier, L. Ricard, F. Mathey, Eur. J. Org. Chem., 1998, **11**, 2683-2687.
19 a) R. Appel, S. Korte, M. Halstenberg, F. Knoch, Chem. Ber., 1982, **115**, 3610-3617. b) for a recent example, see: T. Moeller, P. Wonneberger, M. B. Sarosi, P. Coburger, E. Hey-Hawkins, Dalton Trans., 2015, DOI: 10.1039/C5DT02564H.
20 ORCA - An ab initio, DFT and semiempirical SCF-MO package. Written by F. Neese, Max Planck Institute for Bioinorganic Chemistry, D-45470 Mülheim/Ruhr, 2012. Version 3.0.2. Web page: http://www.cec.mpg.de/forum/portal.php. F. Neese, WIREs Comput Mol Sci 2012, **2**, 73–78.
21 A. D. Becke, J. Chem. Phys., 1993, **98**, 5648-5652. Lee, C. T. Yang, R. G. Parr, Phys. Rev. B, 1988, **37**, 785-789.
22 F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys., 2005, **7**, 3297-3305.
23 a) A. Schaefer, H. Horn, R. Ahlrichs, J. Chem. Phys., 1992, **97**, 2571-2577. b) C. Schaefer, R. Huber, J. Ahlrichs, Chem. Phys. 1994, 100, 5829-5835.
24 D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, Theor. Chim. Acta, 1990, **77**, 123-141. ECP parameters for

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.

25 a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys., 2010, **132**, 154104-154119. b) S. Grimme, S. Ehrlich, L. Goerigk, J. Comput. Chem., 2011, 32, 1456–1465.

26 a) A. Klamt, G. Schüürmann, J. Chem. Soc. Perkin Trans. 2, 1993, **220**, 799-805; b) A. Klamt, J. Phys. Chem. 1995, **99**, 2224-2235.

27 A. Bergner, M. Dolg, W. Kuchle, H. Stoll, Preuss, H. Mol. Phys. 1993, **80**, 1431–1441. Obtained from the EMSL Basis Set Library at https://bse.pnl.gov/bse/portal. D. Feller, J. Comp. Chem., 1996, 17, 1571-1586.

28 C. Riplinger, B. Sandhoefer, A. Hansen, F. Neese, J. Chem. Phys., 2013, **139**, 134101-134113.

29 a) S. Grimme, J. Chem. Phys., 2003, **118**, 9095–9102; b) S. Grimme, L. Goerigk, F. F. Reinhold, WIREs Comput. Mol. Sci., 2012, **2**, 886-906.

30 a) H. P. Kelly, *Phys. Rev.*, 1964, **134**, A1450-A1453; b) W. Meyer, *J. Chem. Phys.*, 1973, **58**, 1017-1035; c) R. Ahlrichs, H. Lischka, V. Staemmler, W. Kutzelnigg, *J. Chem. Phys.*, 1975, **62**, 1225-1234; d) C. Kollmar, F. Nesse, *Mol. Phys.*, 2010, **108**, 2449-2458.

31 F. Wennmohs, F. Neese, Chem. Phys., 2008, **343**, 217–230.

32 a) F. Neese, A. Hansen, F. Wennmohs, S. Grimme Acc. Chem. Res., 2009, **42**, 641-648; b) F. Neese, F. Wennmohs, A. Hansen J. Chem. Phys., 2009, **130**, 114108-114118.

33 a) L. Goerigk and S. Grimme J. Chem. Theory Comput., 2011, **7**, 291; b) ibid. Phys. Chem. Chem. Phys., 2011, **13**, 6670.

Table of contents

CPh_3 as a functional group in P-heterocyclic chemistry: elimination of $HCPh_3$ in the reaction of *P*-CPh_3 substituted Li/Cl phosphinidenoid complexes with $Ph_2C=O$

C. Murcia García,[a] A. Espinosa Ferao,*[b] G. Schnakenburg[a] and R. Streubel*[a]

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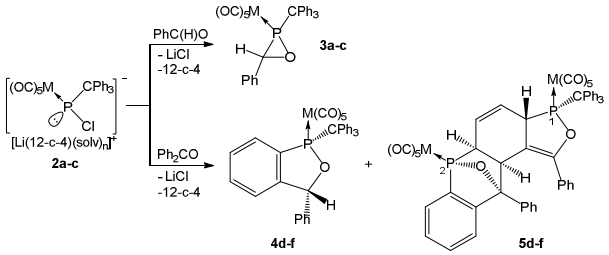
Reaction of Li/Cl phosphinidenoid complexes **2** (M = Cr, Mo, W) react differently with benzaldehyde or benzophenone. The latter resulted in the formation of complexes **4** and **5**, the former bearing a benzo[c]-1,2-oxaphospholane and the latter a novel pentacyclic P-ligand thus also revealing elimination of $HCPh_3$.



[a] Institut für Anorganische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Str. 1, D-53121 Bonn, Germany. Fax: (49)228-739616; Tel: (49)228-735345; e-mail: r.streubel@uni-bonn.de.

[b] Departamento de Química Orgánica, Facultad de Química, Universidad de Murcia, Campus de Espinardo, E-30071 Murcia, Spain. Fax: (34)868-884149; Tel: (34)868-887489; e-mail: artuesp@um.es.

† 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/c000000x/