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# Rearrangement and deoxygenation of 3,3-bis(2-pyridyl)oxaphosphirane complexes



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# Rearrangement and deoxygenation of 3,3-bis(2-pyridyl)oxaphosphirane complexes

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Reaction of Li/Cl phosphinidenoid pentacarbonylmetal(0) complexes **2a-c** (R = $CH(SiMe_3)_2$; M = Cr, Mo, W) with bis(2-pyridyl)ketone led to overcrowded 3,3-bis(2-pyridyl)oxaphosphirane complexes **3a-c.** On heating (pyridine at 95°C or THF at 60°C) **3c** was transformed into complex **4c** having a novel heterobicyclic P-ligand. In case of the *P*-Cp* derivative **2d** the reaction led to a mixture of oxaphosphirane complex **3d** and complex **4d**, whereas only the novel heterobicyclic complex **4e** was formed in case of the *P*-$CPh_3$ substituted complex **2e**. Single-crystal X-ray analysis of **4e** confirmed the structure of the new ligand as to be an isomer of the oxaphosphirane which rearranged under loss of aromaticity of one pyridyl substituent. DFT calculations on *P*-Me model derivative **3f** revealed that, despite the easier C-O bond cleavage in oxaphosphirane complex **3**, only the P-C bond cleavage intermediate **6** enables kinetically favoured P-N ring closure to give the bicyclic P-ligand in **4**. Preliminary studies demonstrated that complex **3c** reacts with an *in situ* generated Ti(III) complex to give phosphaalkene complex **10c**, the hetero-dinuclear complex **10c**·$ZnCl_2$ and the *P,N*-chelate complex **11c**.

## Introduction

In 1990, Mathey *et al.* reported the first synthesis of oxaphosphirane complexes via epoxidation of phosphaalkene complexes.[1] Since then new synthetic methods[2] were continuously developed, but due to various synthetic problems of all methods,[1,3] *e.g.* acid formation as by-product,[1] or rearrangements due to elevated temperatures ("high temperature route")[2e,2f,3b,3c] or the required Cu(I) catalyst,[3a] the chemistry was hampered by lengthy and overall low yield protocols. These problems were recently solved by the advent of a new facile method,[2b,2d,4] *i.e.*, the reaction of Li/Cl phosphinidenoid complexes, which react with carbonyls at low temperatures ("low temperature route"). This enabled synthesis and, hence, systematic study of a broad range of oxaphosphirane complexes, obtained with high diastereoselectivity and good yields. Especially the mild conditions enabled the systematic study of new derivatives, *e.g.* having unsaturated functional groups,[5] *C*-fluorinated phenyls[6] or *C*-spiro units.[7] Recently, we described the synthesis of the first *C*-functionalized oxaphosphirane complex having a *C*-2-pyridyl substituent, possessing an N-donor center well suited for coordination.[8] Whereas in the latter case no ring expansion occurred, *C*-acyl substituted derivatives have revealed some tendency to form a 1,3,2-dioxaphosphol-4-ene ligand system.[9] This result stimulated us to investigate the chemistry of bulky substituted oxaphosphirane complexes having adjacent π-systems and, additionally, donor centres to probe the reactivity towards thermal stability and potential intramolecular ligand substitution as well as deoxygenation reactions.

Herein, we present synthesis and rearrangement of 3,3-bis(2-pyridyl)oxaphosphirane complexes as well as in-depth DFT studies on the rearrangement of model complexes. Furthermore, preliminary results on the reductive SET-induced deoxygenation of *C,C*-disubstituted oxaphosphirane complexes are reported.

## Results and discussion

### Synthesis

Reaction of dichloro(organo)phosphane complexes **1a**-**c**[10] (R = $CH(SiMe_3)_2$) with $^t$BuLi at -78°C in the presence of crown ether generated Li/Cl phosphinidenoid complexes **2a**-**c** (Scheme 1) which, upon addition of three equivalents bis(2-pyridyl)ketone yielded oxaphosphirane complexes **3a**-**c** in high selectivity (Table 1). Despite this **3a**-**c** were only obtained in moderate isolated yields. It was discovered that the main work-up problem was to separate crown ether, LiCl, and the excess of the employed ketone from the products via column chromatography. At this point, it can be only assumed that the nitrogen centres of **3a-c** coordinate to the lithium cation (or to LiCl) and, hence, potentially also to the crown ether thus complicating the separation. This is somehow supported by a

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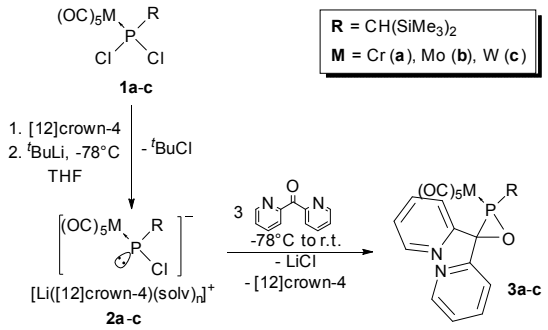
Electronic Supplementary Information (ESI) available: Energetics for the computed mechanism at different computational levels; computed geometries (Cartesian coordinates) and energies for all computed species. See DOI: 10.1039/x0xx00000x

related kind of chelation, *e.g.* for bis(2-pyridyl)methane and LiCl in THF.[11] Despite this, complexes **3a,c** could be obtained in pure form after several recrystallizations.

Close inspection of the NMR spectra revealed that no P-C atropisomerism was observed for complexes **3a**-**c** which is in contrast to mono(2-pyridyl) substituted oxaphosphirane complexes.[8] This difference can be related to the increased steric demand of the two carbon substituents at the ring thus forcing the P-substituent to switch to the unusual *s-trans* conformation to the W-P-C-H moiety. Table 1 displays the chemical shifts of **3c** as well as the J(W,P) coupling constant, being in the expected range for oxaphosphirane complexes.




**Scheme 1**: Reaction of Li/Cl phosphinidenoid complexes **2a**-**c** with bis(2-pyridyl)ketone to give oxaphosphirane complexes **3a**-**c**.

**Table 1** $^{31}$P NMR data (THF) of **3a**-**c**

| Complexes 3 | $\delta^{31}$P [ppm] | $^{1}J_{W,P}$ [Hz] | $^{2}J_{P,H}$ [Hz] | Isolated yield (%) |
|---|---|---|---|---|
| **a** (Cr) | 103.3 | - | 16.4 | 43 |
| **b** (Mo) | 75.8 | - | 14.8 | - |
| **c** (W) | 50.8 | 308.9 | 16.6 | 18 |

The single-crystal X-ray analysis of **3a** confirmed constitution and conformation (Figure 1). As the values for bond lengths and angles are very close to those of previously reported oxaphosphirane complexes, they shall not be discussed further.

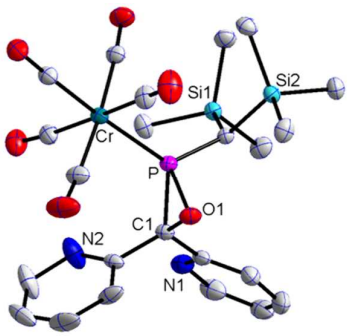
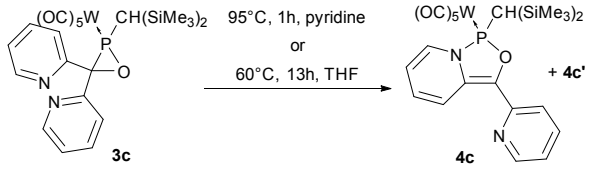



**Figure 1**: Molecular structure of **3a**; 50% probability level; hydrogen atoms are omitted for clarity; selected bond lengths (Å) and angles (°): Cr-P 2.3383(4), P-O1 1.6748(11), C1-O1 1.4658(17), P-C1 1.8066(14), P-O1-C1 69.87(7), C1-P-O1 49.62(6), O1-C1-P 60.50(7).

As the quest for an intramolecular ring expansion of oxaphosphirane complexes was looming since its first observation,[9] we decided to continue this study here using complex **3c** as a case in point. We examined pyridine and THF solutions of **3c** which yielded product mixtures of very similar contents: **3c** underwent rapid ring expansion at elevated temperatures to yield **4c** and **4c'** together with an isomer of unknown constitution (Scheme 2); see also the computational part.

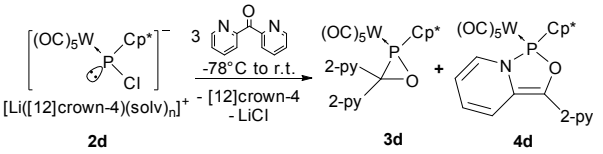



**Scheme 2**: Thermal rearrangement of **3c** to bicyclic ligand complexes **4c,4c'**.

In case of pyridine solutions (95 °C), most of complex **3c** was converted after 1 h and only 3 % of **3c** resided (according to $^{31}$P NMR signal integration). At this point, 63 % of a mixture of s-*cis* and s-*trans* atropisomers of **4c**,**4c'** (see discussion beforehand) was formed (**4c**: $\delta^{31}$P = 170.3 ($^{1}J_{W,P}$ = 318.3 Hz); **4c'**: $\delta^{31}$P = 176.8 ($^{1}J_{W,P}$ = 319.5 Hz). Under these conditions also small amounts of by-products (all together 19%) and 15 % of a minor product ($\delta^{31}$P = 153.4; $^{1}J_{W,P}$ = 326.4 Hz) was formed; unfortunately, separation of the major products by column chromatography failed.

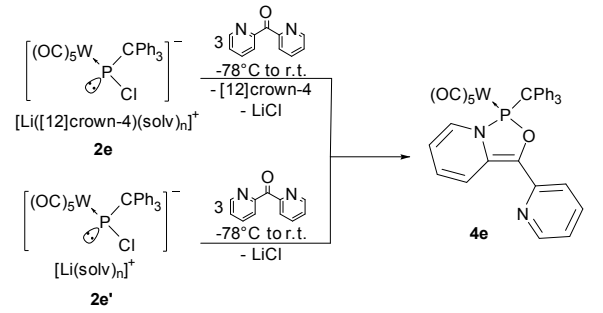
Changing the solvent to THF did improve the reaction outcome. After heating at 60 °C for a total of 13 h, **3c** was almost fully consumed (1 % remaining), but only 66 % of **4c,4c'** were formed together with several by-products, among which was also the by-product at 153.4 ppm (24 %). Attempts to separate these products using column chromatography were not entirely successful and, therefore, only a mixture was obtained having a content of 81 % of **4c,4c'** which was then used for characterization. The MS, IR and NMR characteristic data ($^{31}$P, $^{29}$Si, $^{13}$C{$^{1}$H} and $^{1}$H NMR) could be obtained, providing the first evidence of a rearranged oxaphosphirane ligand. Especially, the appearance of resonances in the $^{1}$H NMR spectra in the range of 5.61-6.92 ppm (4H according to integration) together with resonances in the range of 106.0-131.4 ppm in the $^{13}$C{$^{1}$H} NMR spectra indicated a non-aromatic, conjugated system in **4c,4c'**.

In order to overcome some of the isomer problems and with the hope for a general improvement, the reaction of phosphinidenoid complex **2d**[2d] (R = Cp*) was investigated. The reaction of **2d** with bis(2-pyridyl)ketone yielded complex **3d** as main product (75 %) and about 6 % of **4d** (ratio 1.0:0.1) (Scheme 3). The $^{31}$P{$^{1}$H} NMR chemical shift of the by-product **4d** ($\delta^{31}$P: 171.2, $^{1}J_{W,P}$ = 320.7 Hz) and selected $^{1}$H NMR data led to the conclusion that a complex was formed containing the same bicyclic P-ligand system as in **4c**. Again, all attempts to isolate **3d** and **4d** using column chromatography and recrystallization were unsuccessful. Nevertheless, relevant IR and MS data could be obtained from crude products, including the 1H NMR data of **3d** and **4d** concerning the range of aromatic proton resonances and those of conjugated C,C bonds.




**Scheme 3**: Reaction of Li/Cl phosphinidenoid complex **2d** (R =Cp*) with bis(2-pyridyl)ketone to yield **3d** and **4d** (**3d**:**4d** = 1.0:0.1).

Thus the question arose if this new reaction pathway may originate from an accumulated steric demand of the substituents at phosphorus and the ketone. Therefore, we decided to investigate the case of phosphinidenoid complex **2e**[2a] bearing the even bulkier trityl substituent (R = $CPh_3$) at phosphorus. In this case, no oxaphosphirane complex formation was observed; instead, complex **4e** was formed (63 %) together with some by-products (27 %) of unknown constitution (Scheme 4). But to our great disappointment, the main and somehow common obstacle for all remained, because **4e** could not be obtained in pure form using column chromatography.




**Scheme 4**: Reaction of Li/Cl phosphinidenoid complexes **2e** and **2e'** *(*R =$CPh_3$) with bis(2-pyridyl)ketone to yield **4e**.

Therefore and because it was noticed before that the *P*-trityl substituted Li/Cl phosphinidenoid complex **2e** can be generated even in the absence of [12]crown-4,[2a] we used this protocol hoping to avoid the severe separation problems described. Indeed, using a THF solution of complex **2e'** (no [12]crown-4 present) and three eq. of the ketone complex **4e** was formed selectively and, consequently, isolation was achieved this time using column chromatography. A comparison of the $^{31}P\{^1H\}$ NMR data of **4c-e** revealed a very good agreement (Table 2) thus lending further support; chemical shifts of **4c**/**4c'** were observed at lower field compared to **4d,e**.

**Table 2** $^{31}P\{^1H\}$ NMR data of the bicyclic complexes **4c-e** in reaction solution (THF).

| R | Complex | $\delta^{31}$**P** [ppm] | $^1J_{W,P}$ [Hz] | ratio |
|---|---|---|---|---|
| **$CH(SiMe_3)_2$** | **4c** | 176.8 | 319.5 | 1.0 |
| | **4c'** | 170.3 | 318.3 | 0.4 |
| **Cp*** | **4d** | 171.2 | 320.7 | - |
| **$CPh_3$** | **4e** | 171.2 | 316.4 | - |

The structure of complex **4e** was finally confirmed by single-crystal X-ray diffraction studies (Figure 2), and the endocyclic bond lengths within the bicyclic ligand framework clearly revealed the transformation of one of the pyridyl substituents. Whereas C2-C8 (1.442(7) Å) and C9-C10 (1.437(8) Å) are shorter than a typical C,C-single bond, C8-C9 (1.345(8) Å) and C10-C11 (1.325(7) Å) are close to a C-C double bond and, hence, represent a conjugated π-system. A close inspection of the bond lengths along the bicyclic structure and the pyridyl substituent ruled out the possibility suggested by theoretical calculations (*vide infra*) of an isomer resulting from P-C ring closure, that would interchange positions of N1↔C8 and rotate the heteroaryl group (C1-C3 rotation). In particular, the refinement of the X-ray structure with interchanged N1-C8 positions led to significant higher R values and unrealistic thermal ellipsoids, which ruled out the possibility described before.

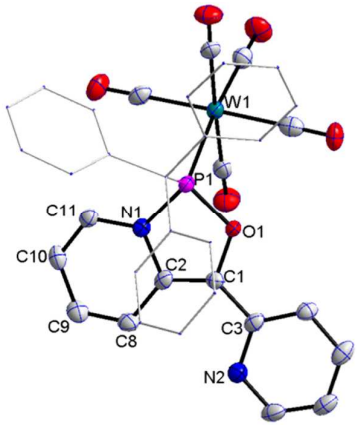
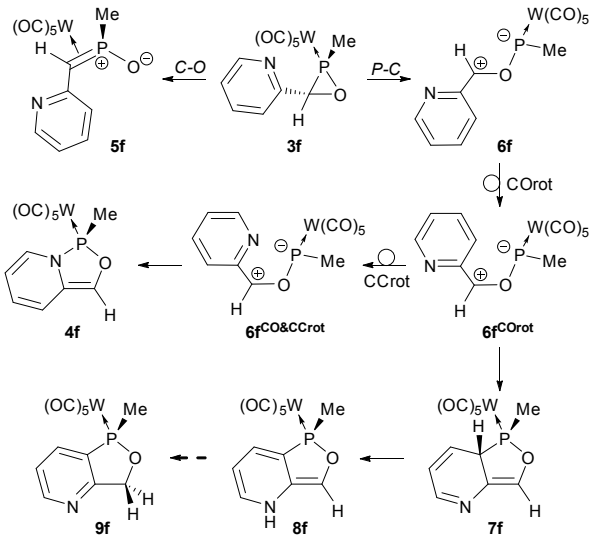



**Figure 2**: Molecular structure of **4e**; 50% probability level; hydrogen atoms are omitted and the trityl group is represented in thin grey lines for clarity; selected bond lengths (Å) and angles (°): W1-P1 2.4799(13), P1-O1 1.632(3), P1-N1 1.712(4), N1-C2 1.418(6), C1-C2 1.346(7), C2-C8 1.442(7), C8-C9 1.345(8), C9-C10 1.437(8), C10-C11 1.325(7), O1-P1-N1 91.01(19), P1-N1-C2 111.6(3), N1-C2-C1 111.2(5), C2-C1-O1 111.9(4), C1-O1-P1, 114.0(3).

Quantum chemical calculations were undertaken in order to unveil the mechanistic path for the conversion of **3** into the final bicyclic complexes **4** as well as the existence of possible isomeric by-products. For the sake of simplicity and computational efficiency a simplified model complex **3f** bearing a *P*-methyl substituent and only one 2-pyridyl group at the ring 3-position (both in relative *trans* configuration), was used as starting point. First of all the possibility of alternative coordination modes of the tungsten(0) carbonyl fragment in **3f** was explored. The isomer with $W(CO)_5$ shifted to N (**3f**$^{N}$) and the *P,N*-$W(CO)_4$ chelate (**3f**$^{PN}$) were found to be 10.41 and 13.43 kcal/mol less stable than **3f**, respectively at the highest level of theory (see the computational details). Next, the two typical endocyclic bond cleavage processes in oxaphosphirane rings[12] were evaluated. In agreement with our previous report, the C-O bond cleavage of **3f** leading to side-on complex **5f** (Scheme 5) is exergonic (Figure 3) and kinetically favoured with regard to the rather endergonic P-C bond cleavage path affording **6f**. Therefore, the stable endocyclic bond cleavage

product **5f** that does not evolve further and is in equilibrium with the unstable (hence reactive) product **6f**.



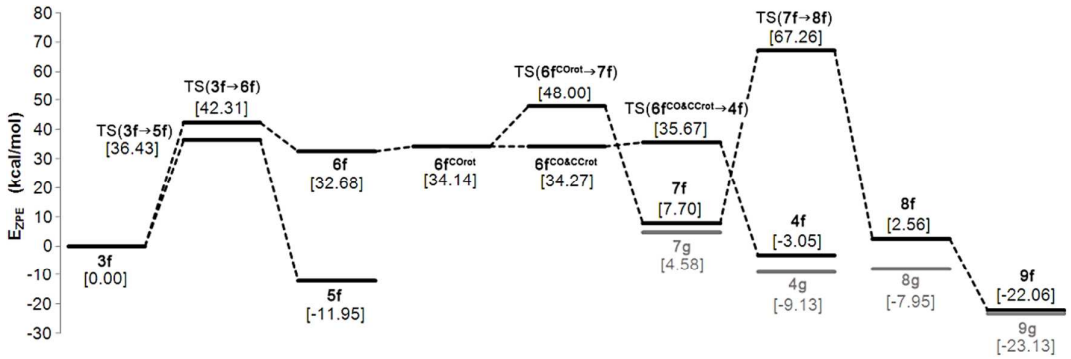

**Scheme 5**: Proposed mechanistic paths for the ring cleavage and expansion of model oxaphosphirane complex **3f**.

The zwitterionic intermediate **6f** bears the positive charge efficiently spread over the 2- (N atom), 4- and 6-positions of the 2-pyridyl substituent which opens up the possibility of cyclization by nucleophilic attack of the negatively charged P atom (Löwdin charge $q^L$ = 0.476 *e*; compare with $q^L$ = 0.751 *e* in **3f** and $q^L$ = 0.620 *e* in **5f**) to one of the aryl *ortho*-positions.

Thus, sequential C-O and C-aryl bond rotations[14] lead to conformer $\mathbf{6f}^{\mathbf{CO\&CCrot}}$ that exergonically cyclizes to the final model complex **4f**, following an almost barrierless path. The C-O bond rotation in **6f** is just an artefact required in intermediates derived from monoaryl substituted model complex **3f,** but it is not needed in intermediates derived from real diaryl substituted complexes **3a-d** (or in case of model complex **3g**, *vide infra*).

The overall transformation **3f**→**4f** turned out to be just slightly exergonic. From the initial C-O bond rotation conformer $\mathbf{6f}^{\mathbf{COrot}}$, P-C ring closure affords complex **7f** which can further evolve to **8f** following a high barrier [1,5]H shift process. This in turn (or **7f**) can undergo a [1,3]H shift to the benzylic position (original carbonyl atom) that would furnish the most stable isomer **9f**. Nevertheless, neither **7f** nor **9f** are compatible with the experimentally found structure **4e** (Figure 2) featuring a totally planar bicyclic moiety with coplanar (2-pyridiyl) substituent. Furthermore the above described energetics would point to **4f** as the most likely final product in comparison to **8f** not only due to its higher stability, but also owing to the quite remarkable energetic barrier (ca. 60 kcal/mol) in the path leading to **8f**. It is worth mentioning that the positive charge developed in both transition states leading to **5f** and **6f** (TS(3f→5f) and TS(3f→6f), (Figure 3) should be expected to be additionally stabilized in real systems **3a-e** bearing two aryl substituents at the ring C atom. In accordance to recent studies on related 3,3-diphenyl substituted systems,[15] these two TS energies should decrease below 30 and 40 kcal/mol, respectively.

**Figure 3**: Computed ($COSMO_{THF}$/DLPNO-CCSD(T)/def2-TZVPPecp) ZPE-corrected energy profile for the conversion of model complex **3f** into **4f** and alternative isomers **7-9f**. In grey the relative energies for final products derived from **3g**.



The aforementioned report also points to a significant relative stabilization of the P-C bond cleavage product together with a destabilization of that resulting from P-O bond cleavage, in this later case due to steric crowding.

Moreover, as the actual relative stabilities between isomers **4** and **8** are expected to depend on additional intramolecular interactions provided by the substituent at the five-membered ring, a new model complex **3g** bearing two (instead of one) 2-pyridyl substituents at C and the corresponding final complexes **4g** and **7-9g** (derived from **3g**) were also computed (Figure 3). Complex **4g** (Figure 4) turned out to be only 1.18 kcal/mol more stable than **8g** at the working level of theory (compare to the difference of 5.61 kcal/mol in case of **4f**/**8f**). This decrease in energy difference arises from the most efficient N-H···N hydrogen bonding in **8f** (d = 2.101 Å) than the C-H···N type in **4f** (d = 2.465 Å).

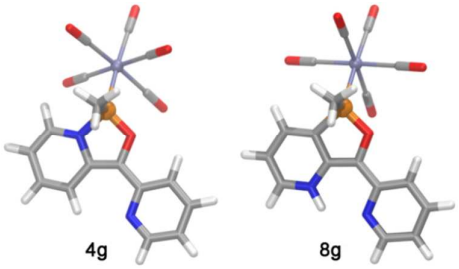
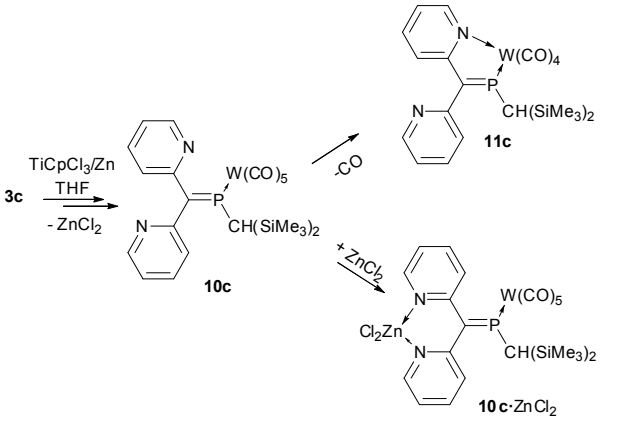



**Figure 4**: Computed ($COSMO_{THF}$/B3LYP-D3/def2-TZVPecp) structures for ring-expansion products derived from model complex **3g**.

Overall, according to the DFT results the loss of aromaticity (of one pyridyl group) in final bicyclic products **4** is energetically compensated by the release of ring strain in the corresponding oxaphosphirane complex precursor **3**. All final energies were computed at some other representative levels of theory for the sake of comparison. For the set of sixteen structures (minima and TSs) derived from **3f** and using the highest DLPNO-CCSD(T) level as reference, rather small root-mean square deviation (rmsd) values were obtained for LPNO/NCEPA1 (0.62 kcal/mol), whereas a slightly lower accuracy resulted from SCS-MP2 (0.90 kcal/mol) and PWPB95-D3 (1.10 kcal/mol) methods (see the ESI).

In previous studies it was shown that reductive SET deoxygenation reactions using Ti(III) complexes yield phosphaalkene complexes, but that the reaction is sensitive towards sterically demanding C-substituents and/or Ti(III) reagents. Furthermore and more recently, formation of *P,N*-chelate phosphaalkene complexes was observed in case of *3*-mono(2-pyridyl) substituted oxaphosphirane complexes.[8] Therefore, it was decided to look into this unusual reaction again, using the new *3,3*-bis(2-pyridyl) substituted derivatives hoping for new insights due to the presence of two N-donor centres.

Hereafter, preliminary results on the reaction of tungsten complex **3c** with the $TiCpCl_3$/Zn system in THF is described. Using reaction conditions described before,[8,15] deoxygenation yielded phosphaalkene complex **10c**, selectively (Scheme 6). This may point to the relief of steric strain in the reagent **3c** (back-strain effect). According to $^{31}P\{^1H\}$ NMR reaction monitoring about 93 % of **10c** and 1 % of the *P,N*-chelate complex **11c** were formed after 25 min, and only 3 % of the oxaphosphirane complex **3c** stayed unreacted. After additional 16 hours, **3c** was completely consumed with **11c** amounting to 11 %, and the conversion to **11c** progressed to reach a maximum content of 22 % after 24 days, and 69 % of **10c** remained. Out of this solution, crystals were obtained that were suitable for X-ray diffraction studies.




**Scheme 6**: Reaction of oxaphosphirane complex **3c** with $TiCpCl_3$/Zn in THF.

This somehow puzzling finding prompted us to inspect more closely the $^{31}P\{^1H\}$ NMR signals of **10c** ($\delta^{31}P$: 264.6 ppm, $^1J_{W,P}$ = 287.7 Hz) and **11c** ($\delta^{31}P$: 308.5 ppm, $^1J_{W,P}$ = 274.3 Hz). Line shape analysis revealed a broad signal for **10c** (FWHM ≈ 20 Hz) compared to **11c** (FWHM ≈ 2 Hz), thus indicating a dynamic process in which **10c** is involved, but **11c** is not. One more aspect deserves mention: the $^{31}P$ resonance for **10c** was shifted to lower field by about 20 ppm compared to the mono(2-pyridyl) tungsten complex.[8] This relatively large shift brought up the idea that complex **10c** was actually formed together with some unknown amounts of hetero-dinuclear phosphaalkene complex **10c**·$ZnCl_2$; the formation of which also stopping the further conversion of **10c** into **11c**.

The result of the X-ray diffraction study revealed the structure of the hetero-dinuclear complex **10c**·$ZnCl_2$ possessing a $ZnCl_2$ unit bound in an *N,N*-chelate fashion by the two nitrogen centres (Figure 5). A similar *N,N*-coordination mode (of the dipyridyl subunit) has been previously described for the complex formed by bis(2-pyridyl)ketone and $ZnCl_2$ in THF.[16] Comparable to this known *N,N*-chelate Zn(II) complex,[16] a pseudo-tetrahedral coordination sphere at the Zn(II) centre in **10c**·$ZnCl_2$ with a relatively large Cl1-Zn-Cl2 (116.27(4)°) and small N1-Zn-N2 (92.6(1)°) angle was observed.

Despite being preliminary, the outcome of this study on the SET reaction shed light on two interesting aspects: (1) $ZnCl_2$ present in the reductive deoxygenation of oxaphosphirane complexes might not be innocent, especially if it can coordinate to N-centres as in the present case. It might even participate in (or enhance) oxaphosphirane ring activation. Fur-

thermore, it also reveals (2) why no full conversion of **10c** into the *P,N*-chelate complex **11c** was observed. Especially as the latter formation is not reversible under these conditions. But there is also an open question remaining: apparently, $ZnCl_2$ is not fully available (after formation of $[TiCpCl_2]_2$), for the complexation of the phosphaalkene complex to occur effectively right after its formation – which in principle it should. So why? Further intense studies are required to get a better understanding.

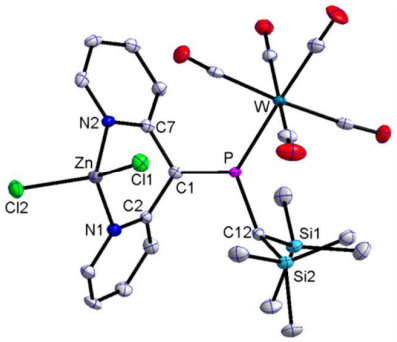



**Figure 5**: Molecular structure of **10c**·$ZnCl_2$; 50% probability level; hydrogen atoms are omitted for clarity; selected bond lengths (Å) and angles (°): W–P 2.4772(10), P–C1 1.681(4), P–C12 1.814(4), C1–C2 1.489(5), C1–C7 1.494(5), Zn-N1 2.058(3), Zn-N2 2.066(3), C1–P–W 124.71(14), C1–P–C12 108.13(19), C2-C1-C7 115.3(3), N1–Zn–N2 92.69(13).

## Experimental

### Synthetic procedures

All reactions were carried out under an atmosphere of inert gas using purified and dried argon and standard Schlenk techniques. Solvents were dried over sodium wire/benzophenone and distilled (and stored) under argon. NMR data were recorded on a Bruker DMX 300 spectrometer at 25 °C using $C_6D_6$, $CDCl_3$, THF-$d^8$ or THF as solvent; chemical shifts are given in ppm relative to tetramethylsilane ($^1$H: 300.13, $^{13}$C: 75.5, $^{29}$Si: 59.6 MHz), and 85% $H_3PO_4$ ($^{31}$P: 121.5 MHz). Mass spectra were recorded on a MAT 95 XL Finnigan (EI, 70 eV, $^{184}$W, $^{52}$Cr) spectrometer, and IR spectra were recorded on a Thermo Nicolet 380 FT-IR spectrometer with attenuated total reflection (ATR) attachment; selected data are given only. Melting points were determined using a Büchi apparatus; the values are not corrected. Elemental analyses were performed using an Elementar VarioEL instrument.

### Synthesis of dichloro(organo)phosphane complexes

Dichloro(organo)phosphane complexes (R = $CH(SiMe_3)_2$, Cp*, $CPh_3$) were synthesized according to the literature methods.[2a,10,17]

### Synthesis of complexes 3a-c

To a solution of 0.5 g (0.853 mmol) of **1a**-**c** (**a**: 1.10 mmol, **b**: 1.01mmol, **c**: 0.853 mmol) and 1.0 equivalent of [12]crown-4 (**a**: 177.9 µL, **b**:163.4 µL, **c**: 138.2 µL) in 15 mL THF, cooled to -90°C, 1.0 equivalent $^t$BuLi (**a**: 0.65 mL, **b**: 0.59 mL, **c**: 0.53 mL, 1.7 M in *n*-pentane) were added dropwise and stirred for 5 minutes. Then 3 equivalents bis(2-pyridyl)ketone (**a**: 0.60 g, **b**: 0.56 g, **c**: 0.47 g) were added. The solution was allowed to warm to ambient temperature over 3 hours stirring. The solvent was removed *in vacuo* ($\sim 10^{-2}$ mbar) and the product extracted with *n*-pentane and 10% diethyl ether (10 x 20 mL, **b**: under exclusion from light). The product was then purified by column chromatography ($Al_2O_3$, -20°C, **a**: ø = 3 cm, h = 3 cm, eluent: petroleum ether and up to 20% diethyl ether, **b**: under exclusion from light, ø = 3 cm, h = 2 cm, eluent: petroleum ether and up to 10% diethyl ether, **c**: ø = 1 cm, h = 1 cm, eluent: petroleum ether). Recrystallization from *n*-pentane yielded **3a**,**c** as solids, **3b** could not be obtained in pure form due to decomposition during purification.

**Complex 3a: [Cr(CO)$_5${Me$_3$Si)$_2$CH-PC(C$_5$H$_4$N)$_2$-O}].** Yellow solid, yield: 0.269 g (0.475 mmol, 43%); m.p. 115°C; $^1$H NMR ($C_6D_6$): δ = 0.06 (s, 9H, $SiMe_3$), 0.42 (s, 9H, $SiMe_3$), 1.53 (d, $^2J_{P,H}$ = 16.3 Hz, 1H, C*H*($SiMe_3$)$_2$), 6.45 (dd, $^{3,4}J_{H,H}$ = 4.9 Hz, 7.0 Hz, 1H, C*H*$_{Py}$), 6.58-6.63 (m, 1H, C*H*$_{Py}$), 6.94-7.03 (m, 2H, C*H*$_{Py}$), 7.56 (d, $^3J_{H,H}$ = 7.7 Hz, 1H, C*H*$_{Py}$), 7.79 (d, $^3J_{H,H}$ = 7.9 Hz, 1H, C*H*$_{Py}$), 8.31 (d, $^3J_{H,H}$ = 4.1 Hz, 1H, C*H*$_{Py}$), 8.49 (d, $^3J_{H,H}$ = 4.1 Hz, 1H, C*H*$_{Py}$); $^{13}$C{$^1$H} NMR ($C_6D_6$): δ = 1.48 (d, $^3J_{P,C}$ = 4.4 Hz, $SiMe_3$), 2.1 (d, $^3J_{P,C}$ = 2.7 Hz, $SiMe_3$), 27.1 (d, $^1J_{P,C}$ = 45.3 Hz, *C*H($SiMe_3$)$_2$), 70.9 (d, $^1J_{P,C}$ = 17.6 Hz, *C*(P)(O)), 122.5 (s, *C*H$_{Py}$), 123.2 (d, $^5J_{P,C}$ = 0.9 Hz, *C*H$_{Py}$), 123.6 (s, *C*H$_{Py}$), 124.8 (d, $^2J_{P,C}$ = 3.8 Hz, *C*H$_{Py}$), 135.9 (s, *C*H$_{Py}$), 136.5 (s, *C*H$_{Py}$), 149.2 (s, 2 *C*H$_{Py}$), 157.7 (s, *C*$_{Py}$), 158.2 (d, $^2J_{P,C}$ = 2.8 Hz, *C*$_{Py}$), 215.3 (d, $^2J_{P,C}$ = 15.2 Hz, *cis*-CO), 219.3 (d, $^2J_{P,C}$ = 3.5 Hz, *trans*-CO); $^{29}$Si NMR ($C_6D_6$): δ = -2.2 (d, $^2J_{P,Si}$ = 6.7 Hz, $SiMe_3$), 3.8 (s, $SiMe_3$); $^{31}$P NMR ($C_6D_6$): δ = 104.4 ($^2J_{P,H}$ = 16.3 Hz); IR (neat): $\tilde{\nu}$ = 3062, 2963 (w, CH), 2069, 1997, 1951, 1918 (s, CO), 1581, 1568 (m, C=C), 1462, 1429 (m, C=N), 1249 (m, $SiMe_3$); MS: selected data m/z (%) = 566.1 (11) $[M]^{+\bullet}$, 454.1 (8) $[M\text{-}4CO]^+$, 426.1 (90) $[M\text{-}5CO]^+$, 374.2 (55) $[M\text{-}Cr(CO)_5]^+$, 294.1 (50) $[M\text{-}(Py)_2CO\text{-}Me\text{-}SiMe_3]^+$, 269.1 (12) $[M\text{-}3CO\text{-}CH(SiMe_3)_2\text{-}2HCN]^+$, 242.1 (20) $[M\text{-}3CO\text{-}CH(SiMe_3)_2\text{-}2HCN\text{-}C_2H_3]^+$, 236.0 (30) $[M\text{-}(Py)_2CO\text{-}2SiMe_3]^+$, 215.1 (40) $[M\text{-}Cr(CO)_5\text{-}CH(SiMe_3)_2]^+$, 208.0 (30) $[M\text{-}(Py)_2CO\text{-}2SiMe_3\text{-}CO]^+$, 193.0 (10) $[M\text{-}3CO\text{-}C_4H_4N\text{-}Py\text{-}2SiMe_3]^+$, 73.1 (100) $[SiMe_3]^+$; elemental analysis (%) calculated for $C_{23}H_{27}CrN_2O_6PSi_2$ (%): C 48.75, H 4.80, N 4.94; found: C 47.53, H 5.12, N 4.74.

**Complex 3b: [Mo(CO)$_5${Me$_3$Si)$_2$CH-PC(C$_5$H$_4$N)$_2$-O}].** $^{31}$P NMR (THF): δ = 75.8 ($^2J_{P,H}$ = 14.8 Hz).

**Complex 3c: [W(CO)$_5${Me$_3$Si)$_2$CH-PC(C$_5$H$_4$N)$_2$-O}].** Light yellow solid, yield: 0.108 g (0.155 mmol, 18%); m.p. 123°C; $^1$H NMR ($C_6D_6$): δ = 0.08 (s, 9H, $SiMe_3$), 0.42 (s, 9H, $SiMe_3$), 1.77 (d, $^2J_{P,H}$ = 16.3 Hz, 1H, C*H*($SiMe_3$)$_2$), 6.48 (dd, $^{3,4}J_{H,H}$ = 4.86 Hz, 7.38 Hz, 1H, C*H*$_{Py}$), 6.60 (dd, $^{3,4}J_{H,H}$ = 4.90 Hz, 7.42 Hz, 1H, C*H*$_{Py}$), 6.94 (td, $^{3,4}J_{H,H}$ = 1.70 Hz, 7.76 Hz, 1H, C*H*$_{Py}$), 7.01 (td, $^{3,4}J_{H,H}$ = 1.62 Hz, 7.72 Hz, 1H, C*H*$_{Py}$), 7.58 (d, $^3J_{H,H}$ = 7.86 Hz, 1H, C*H*$_{Py}$), 7.87 (d, $^3J_{H,H}$ = 7.95 Hz, 1H, C*H*$_{Py}$), 8.30 (d, $^3J_{H,H}$ = 4.0 Hz, 1H, C*H*$_{Py}$), 8.49 (d, $^3J_{H,H}$ = 4.1 Hz, 1H, C*H*$_{Py}$); $^{13}$C{$^1$H} NMR ($C_6D_6$): δ = 1.55 (d, $^3J_{P,C}$ = 4.6 Hz, $SiMe_3$), 2.0 (d, $^3J_{P,C}$ = 2.9 Hz, $SiMe_3$), 25.8 (d, $^1J_{P,C}$ = 38.4 Hz, *C*H($SiMe_3$)$_2$), 71.0 (d, $^1J_{P,C}$ = 21.9 Hz,

*C*(P)(O)), 122.5 (d, $^{5}J_{P,C}$ = 0.6 Hz, *C*H$_{Py}$), 123.1 (d, $^{5}J_{P,C}$ = 0.9 Hz, *C*H$_{Py}$), 123.7 (d, $^{3}J_{P,C}$ = 0.8 Hz, *C*H$_{Py}$), 124.7 (d, $^{3}J_{P,C}$ = 3.9 Hz, *C*H$_{Py}$), 135.8 (d, $^{4}J_{P,C}$ = 0.8 Hz, *C*H$_{Py}$), 136.5 (s, *C*H$_{Py}$), 149.2 (d, $^{4}J_{P,C}$ = 0.9 Hz, *C*H$_{Py}$), 149.3 (s, *C*H$_{Py}$), 157.3 (s, *C*$_{Py}$), 158.3 (d, $^{2}J_{P,C}$ = 2.8 Hz, *C*$_{Py}$), 195.8 (d, $^{2}J_{P,C}$ = 8.2 Hz, *cis*-CO), 196.6 (d, $^{2}J_{P,C}$ = 35.1 Hz, *trans*-CO); $^{29}$Si NMR ($C_6D_6$): δ = -1.9 (d, $^{2}J_{P,Si}$ = 6.9 Hz, SiMe$_3$), 4.0 (s, SiMe$_3$); $^{31}$P NMR ($C_6D_6$): δ = 51.5 ($^{1}J_{W,P}$ = 310.0 Hz, $^{1}J_{P,C}$ = 35.7 Hz, $^{2}J_{P,H}$ = 16.5 Hz); IR (neat): ṽ = 3051, 2985 (m, CH), 2076, 1992, 1925 (s, CO), 1581, 1565 (m, C=C), 1462.6, 1429 (m, C=N), 1255 (m, SiMe$_3$); MS: selected data m/z (%) = 698.1 (35) [M]$^{+\bullet}$, 670.1 (5) [M-CO]$^{+}$, 660.1 (30) [M-C$_3$H$_2$]$^{+}$, 642.1 (20) [M-2CO]$^{+}$, 614.1 (50) [M-3CO]$^{+}$, 586.1 (5) [M-4CO]$^{+}$, 576.1 (50) [M-3CO-C$_3$H$_2$]$^{+}$, 558.1 (80) [M-5CO]$^{+}$, 484.0 (30) [M-2Me-(Py)$_2$CO]$^{+}$, 458.0 (45) [M-(Py)$_2$CO-2CO]$^{+}$, 456.0 (35) [M-2Me-CO-(Py)$_2$CO]$^{+}$, 430.0 (15) [M-3CO-(Py)$_2$CO]$^{+}$, 402.0 (30) [M-(Py)$_2$CO-4CO]$^{+}$, 374.1 (65) [M-W(CO)$_5$]$^{+}$, 358.0 (32) [M-Me-H-5CO-(Py)$_2$CO]$^{+}$, 342.0 (20) [M-2Me-5CO- (Py)$_2$CO+H]$^{+}$, 297.1 (12) [M-W(CO)$_5$-2C$_3$H$_3$+H]$^{+}$, 257.1 (20) [M-W(CO)$_5$-Py-C$_3$H$_3$]$^{+}$, 243.1 (40) [M-W(CO)$_5$-Py-C$_3$H$_3$N]$^{+}$, 215.0 (30) [M-W(CO)$_5$-CH(SiMe$_3$)$_2$]$^{+}$, 73.1 (100) [SiMe$_3$]$^{+}$; elemental analysis (%) calculated for $C_{23}H_{27}N_2O_6PSi_2W$: C 39.55, H 3.90, N 4.01; found: C 39.31, H 4.32, N 3.98.

**Synthesis of complexes 4c,4c'**

A solution of 0.15 g (0.215 mmol) **3c** in 1.5 mL THF was stirred at 60°C for 13h in total. The solvent was removed *in vacuo* (~$10^{-2}$ mbar) and the product was then purified by column chromatography ($Al_2O_3$, -20°C, ø = 1 cm, h = 0.5 cm, eluent: petroleum ether). The first, red coloured fraction, yielded complexes **4c,4c'** (81% by integration of the signals, ratio **4c** : **4c'**= 1.0 : 0.04), but also some by-products as impurities. The NMR, MS and IR data were obtained for this mixture.

**Complex 4c: [W(CO)$_5${(Me$_3$Si)$_2$CHP(C$_5$H$_4$N)$_2$-O}].** $^{1}$H NMR ($CDCl_3$): δ = 0.25 (s, 9H, SiMe$_3$), 0.30 (s, 9H, SiMe$_3$), 1.92 (s, 1H, C*H*(SiMe$_3$)$_2$), 5.61 (dddd, 1H, $J_{H,H}$ = 1.2 Hz, 6.0 Hz, 7.2 Hz, $J_{P,H}$ = 2.2 Hz, C*H*), 6.29-6.39 (m, 1H, C*H*), 6.81-6.92 (m, 2H, C*H*), 7.16-7.21 (m, 1H, C*H*$_{Py}$), 7.54-7.61 (m, 1H, C*H*$_{Py}$), 7.68-7.72 (m, 1H, C*H*$_{Py}$), 8.45 (ddd, $J_{H,H}$ = 0.9 Hz, 1.7 Hz, 4.8 Hz, $J_{P,H}$ = br, 1H, C*H*$_{Py}$); $^{13}$C{$^{1}$H} NMR ($CDCl_3$): δ = 2.72 (d, $^{3}J_{P,C}$ = 2.9 Hz, SiMe$_3$), 2.89 (d, $^{3}J_{P,C}$ = 2.1 Hz, SiMe$_3$), 44.6 (d*, *C*H(SiMe$_3$)$_2$), 106.0 (d, $^{2}J_{P,C}$ = 5.9 Hz, *C*H), 116.1 (s, *C*H), 118.1 (s, *C*H), 118.7 (d, $^{3}J_{P,C}$ = 1.9 Hz, *C*H$_{Py}$), 128.1 (s, *C*H), 131.4 (d, $^{3}J_{P,C}$ = 12.3 Hz, *C*H), 136.2 (s, *C*H$_{Py}$), 137.1 (d, $^{2/3}J_{P,C}$ = 4.9 Hz, *C*$_q$), 149.2 (s, *C*H$_{Py}$), 149.4 (d, $^{2/3}J_{P,C}$ = 7.9 Hz, *C*$_q$), 151.9 (d, $^{2/3}J_{P,C}$ = 4.5 Hz, *C*$_{Py}$), 196.1 (d, $^{2}J_{P,C}$ = 8.2 Hz, *cis*-CO), *trans*-CO*; $^{29}$Si NMR ($CDCl_3$): δ = -1.2 (d, $^{2}J_{P,Si}$ = 1.7 Hz, SiMe$_3$), -1.0 (d, $^{2}J_{P,Si}$ = 6.9 Hz, SiMe$_3$); $^{31}$P NMR ($CDCl_3$): δ = 176.2 ($^{1}J_{W,P}$ = 321.9 Hz, $J_{P,H}$ = br, 78%, **4c**), 169.1 ($^{1}J_{W,P}$ = 317.8 Hz, $J_{P,H}$ = br, 3%, **4c'**), 152.1 ppm ($^{1}J_{W,P}$ = 330.7 Hz, $J_{P,H}$= 7.1 Hz, 14.5 Hz, (dd), 10%); undefined by-products 7%*; IR (neat): ṽ = 2961, 2924 (w, CH), 2076, 1992, 1932 (s, CO), 1630, 1582, 1544, 1525 (m, C=C), 1466, 1435 (m, C=N), 1256 (SiMe$_3$), 1096, 1063, 1010 (s, PN); MS: selected data m/z (%) = 660.0 (5) [M-C$_3$H$_3$+H]$^{+}$, 576.1 (10) [M-C$_3$H$_3$+H-3CO]$^{+}$, 503.1 (5) [M-C$_3$H$_3$+H-3CO-SiMe$_3$]$^{+}$, 458.0 (5) [M-C$_3$H$_3$+H-2SiMe$_3$-2CO]$^{+}$, 429.1 (5) [M-C$_3$H$_3$+H-2SiMe$_3$-3CO]$^{+}$, 281.1 (5) [M-W(CO)$_5$-Py-Me.
* Intensity too low to identify.

**Synthesis of complexes 3d/4d**

To a solution of 0.5 g (0.891 mmol) of [W(CO)$_5$P(Cp*)Cl$_2$][17c] and 144.2 µL [12]crown-4 (0.891 mmol, 1.0 equivalents) in 15 mL THF, cooled to -90°C, 0.52 mL $^{t}$BuLi (0.891 mmol, 1.0 equivalents, 1.7 M in *n*-pentane) were added dropwise and stirred for 5 minutes at this temperature. Then 0.49 g bis(2-pyridyl)ketone (2.67 mmol, 3 equivalents) were added. The solution was allowed to warm to ambient temperature over 3 hours stirring. The solvent was removed *in vacuo* (~$10^{-2}$ mbar) and the product extracted with *n*-pentane (5 x 20 mL, ratio of **3d**:**4d** = 1.0:0.6). The product mixture was then tried to purify by column chromatography ($Al_2O_3$, -20°C, ø = 1 cm, h = 1 cm, eluent: petroleum ether). A second column chromatography and recrystallization from *n*-pentane could not separate the two products (**3d/4d**) from each other and/or the by-products. So only the crude mixture was analysed.
**Complexes 3d/4d** (ratio 1.0:0.1): $^{1}$H NMR ($CDCl_3$): selected data for **3d**: δ = 7.06 (ddt, $J_{H,H}$ = 7.5 Hz, 4.9 Hz, 1.3 Hz, 1H, C*H*$_{Py}$), 7.14 (ddd, $J_{H,H}$ = 7.5 Hz, 4.8 Hz, 1.2 Hz, 1H, C*H*$_{Py}$), 7.39 (ddd, $J_{H,H}$ = 7.6 Hz, 4.8 Hz, 1.3 Hz, 1H, C*H*$_{Py}$), 7.80 (td, $J_{H,H}$ = 7.7 Hz, 1.7 Hz, 1H, C*H*$_{Py}$), 7.47-7.64 (m, 2H, C*H*$_{Py}$), 8.50 (ddd, $J_{H,H}$ = 4.8 Hz, 1.7 Hz, 0.9 Hz, 1H, C*H*$_{Py}$), 8.56-8.64 (m, 1H, C*H*$_{Py}$); selected data for **4d**: 5.57 (dddd, $J_{H,H}$ = 7.3 Hz, 6.0 Hz, 2.1 Hz, 1.2 Hz, 1H, C*H*), 6.29 (ddt, $J_{H,H}$ = 9.7 Hz, 5.9 Hz, 0.9 Hz, 1H, C*H*), 6.61 (ddt, $J_{H,H}$ = 7.1 Hz, 5.9 Hz, 1.2 Hz, 1H, C*H*), 6.78 (ddd, $J_{H,H}$ = 7.5 Hz, 4.8 Hz, 1.1 Hz, 1H, C*H*), 7.20-7.24 (m, 1H, C*H*$_{Py}$), 8.02 (dt, $J_{H,H}$ = 7.8 Hz, 1.1 Hz, 1H, C*H*$_{Py}$), 8.36 (ddd, $J_{H,H}$ = 4.8 Hz, 1.9 Hz, 0.9 Hz, 1H, C*H*$_{Py}$), 8.67 (ddd, $J_{H,H}$ = 4.8 Hz, 1.7 Hz, 1.0 Hz, 1H, C*H*$_{Py}$); $^{31}$P NMR ($CDCl_3$): **3d**: δ = 51.9 ($^{1}J_{W,P}$ = 309.7 Hz, $J_{P,H}$ = m, 50%); **4d**: δ = 171.2 ($^{1}J_{W,P}$ = 320.7 Hz, $J_{P,H}$ = m, 32%); Ratio of **3d**:**4d** after column chromatography (1.0:0.6); IR (neat, of the mixture): ṽ = 2917, 2853 (w, CH), 2069 (m, CO), 1978, 1914 (w, CO), 1914 (s, CO), 1682, 1583, 1569 (m, C=C), 1466, 1435 (m, C=N), 993 (m, PN); MS: selected data m/z (%) = 674.0 (2) [M]$^{+\bullet}$, 590.1 (1) [M–3CO]$^{+}$, 538.9 (8) [M–Cp*]$^{+}$, 482.9 (5) [M–Cp*-2CO]$^{+}$, 454.9 (5) [M–Cp*-3CO]$^{+}$, 426.9 (1) [M-Cp*-4CO]$^{+}$, 398.9 (5) [M–Cp*-5CO]$^{+}$, 215.0 (1) [M-Cp*-W(CO)$_5$]$^{+}$, 184.1 (15) [M-(CO)$_5$WPCp*]$^{+}$, 156.1 (10) [M-(CO)$_5$WPCp*-HCN-H]$^{+}$, 136.1 (15) [Cp*-H]$^{+}$, 121.1 (22) [Cp*-Me+H]$^{+}$, 105.0 (10) [Cp*-2Me]$^{+}$.

**Synthesis of complex 4e**

To a solution of 0.5 g (0.747 mmol) of [W(CO)$_5$P(CPh$_3$)Cl$_2$][2a] in 15 mL THF, cooled to -90°C, 0.53 mL $^{t}$BuLi (0.896 mmol, 1.2 equivalents, 1.7 M in *n*-pentane) were added dropwise and stirred for 5 minutes at this temperature. Then 0.41 g bis(2-pyridyl)ketone (2.241 mmol, 3 equivalents) were added. The solution was allowed to warm to ambient temperature over 3 hours stirring. The solvent was removed *in vacuo* (~$10^{-2}$ mbar) and the product extracted with *n*-pentane (~140 mL). The product was then purified by column chromatography ($Al_2O_3$, -20°C, ø = 2 cm, h = 4 cm, eluent:

petroleum ether and up to 5% diethyl ether). Recrystallization from *n*-pentane yielded the product as a solid.

**Complex 4e: [W(CO)$_5${Ph$_3$C-PC(C$_5$H$_4$N)$_2$-O}].** Red solid, yield: 0.05 g (0.06 mmol, 9%); m.p. 106°C; $^1$H NMR (C$_6$D$_6$): δ = 4.84 (dd, $^{3,4}J_{H,H}$ = 6.5 Hz, 1H, C*H*), 5.70 (dd, $^{3,3}J_{H,H}$ = 5.9 Hz, 9.6 Hz, 1H, C*H*), 5.99 (dd, $^3J_{H,H}$ = 7.2 Hz, $^4J_{P,H}$ = 4.1 Hz, 1H, C*H*), 6.33 (dd, $^{3,4}J_{H,H}$ = 5.1 Hz, 6.4 Hz, 1H, C*H*), 6.91-6.98 (m, 1H, C*H*$_{Py}$), 6.99-7.12 (m, 6H, C*H*$_{Ph}$), 7.12-7.18 (m, 3H, C*H*$_{Ph}$), 7.21 (dm, 1H, $^{3,4}J_{H,H}$ = 6.2 Hz, C*H*$_{Py}$), 7.74 (dm, $^3J_{H,H}$ = 9.9 Hz, 6H, C*H*$_{Ph}$), 8.21 (d, $^3J_{H,H}$ = 4.1 Hz, 1H, C*H*$_{Py}$); $^{13}$C{$^1$H} NMR (C$_6$D$_6$): δ = 74.1 (d, $^1J_{P,C}$ = 14.3 Hz, *C*Ph$_3$), 107.6 (d, $^2J_{P,C}$ = 2.3 Hz, *C*H), 116.0 (s, *C*H$_{Py}$), 118.1 (s, *C*H), 119.5 (d, $^3J_{P,C}$ = 2.3 Hz, *C*H$_{Ph}$), 127.3 (s, *C*H), 128.3 (s, *C*H$_{Ph}$), 128.4 (s, *C*H$_{Ph}$), 129.5 (d, $^3J_{P,C}$ = 7.9 Hz, *C*H), 129.9 (s, *C*H$_{Py}$), 132.0 (s, *C*$_q$), 132.4 (d, $^2J_{P,C}$ = 2.4 Hz, *C*$_q$), 133.3 (d, $^{2,3}J_{P,C}$ = 11.6 Hz, *C*$_q$), 135.7 (s, *C*H$_{Py}$), 148.9 (s, *C*H$_{Py}$), 151.4 (d, $^3J_{P,C}$ = 4.2 Hz, *C*$_{Py}$), 196.1 (d, $^2J_{P,C}$ = 7.8 Hz, *cis*-CO), 199.2 (d, $^2J_{P,C}$ = 38.2 Hz, *trans*-CO); $^{31}$P NMR (C$_6$D$_6$): δ = 171.8 ($^1J_{W,P}$ = 319.9 Hz); IR (neat): $\tilde{\nu}$ = 2960, 2923 (w, CH), 2076, 1998, 1932 (s, CO), 1629, 1579, 1542, 1524 (m, C=C), 1490, 1467, 1447, 1434, 1423 (m, C=N), 1088, 1062, 1013 (s, PN); MS: selected data m/z (%) = 782.1 (0.2) [M]$^{+\bullet}$, 647.1 (0.2) [M-2CO-HCN-2C$_2$H$_2$]$^+$, 539.0 (2) [M-CPh$_3$]$^+$, 511.0 (1) [M-CO-CPh$_3$]$^+$, 455.0 (4) [M-3CO-CPh$_3$]$^+$, 399.0 (1) [M-5CO-CPh$_3$]$^+$, 243.1 (100) [CPh$_3$]$^+$; 165.1 (80) [CPh$_3$-Ph]$^+$; elemental analysis (%) calculated for C$_{35}$H$_{23}$N$_2$O$_6$P$_2$W (%): C 53.73, H 2.96, N 3.58; found: C 54.64, H 3.82, N 3.55.

### Synthesis of complexes 10c/11c

To a solution of 15.7 mg TiCpCl$_3$ (71.6 µmol) and 5.6 mg Zn (85.6 µmol) in 0.9 mL THF-d$^8$, 50.0 mg (71.6 µmol) of **3c** were added and stirred for 60 hrs at ambient temperature. A mixture of the phosphaalkene complex **10c**·ZnCl$_2$ (27%) and the *P,N*-chelate complex **11c** (32%), besides several by-products (41%) was obtained and submitted for NMR-spectroscopic characterization.

**Complex 10c**·ZnCl$_2$**: [W(CO)$_5${(Me$_3$Si)$_2$CH}P=C(C$_5$H$_4$N)$_2$}]·ZnCl$_2$.** $^1$H NMR (THF-d$^8$): δ = 0.11 (s, 9H, SiMe$_3$), 0.53 (s, 9H, SiMe$_3$), 2.94 (d, $^2J_{P,H}$ = 18.5 Hz, 1H, C*H*(SiMe$_3$)$_2$), 7.67 (dd, $^{3/4}J_{H,H}$ = 7.7 Hz, 1.8 Hz, 2H, C*H*$_{Py}$), 7.59 (d, $^{3/4}J_{H,H}$ = 8.0 Hz, 1H, C*H*$_{Py}$), 7.78 (d, $^{3/4}J_{H,H}$ = 7.6 Hz, 1H, C*H*$_{Py}$), 8.11 (d, $^{3/4}J_{H,H}$ = 7.7 Hz, 1H, C*H*$_{Py}$), 8.20 (d, $^{3/4}J_{H,H}$ = 7.6 Hz, 1H, C*H*$_{Py}$), 8.71 (d, $^{3/4}J_{H,H}$ = 4.7 Hz, 1H, C*H*$_{Py}$), 8.96 (d, $^{3/4}J_{H,H}$ = 4.8 Hz, 1H, C*H*$_{Py}$); $^{13}$C{$^1$H} NMR (THF-d$^8$): δ = 2.5 (d, $^3J_{P,C}$ = 4.6 Hz, SiMe$_3$), 3.0 (d, $^3J_{P,C}$ = 3.3 Hz, SiMe$_3$), 32.6 (d, $^1J_{P,C}$ = 34.8 Hz, *C*H(SiMe$_3$)$_2$), 125.4 (s, *C*H$_{Py}$), 126.3 (s, *C*H$_{Py}$), 127.8 (d, $^{3/4/5}J_{P,C}$ = 6.6 Hz, *C*H$_{Py}$), 129.5 (d, $^{3/4/5}J_{P,C}$ = 9.6 Hz, *C*H$_{Py}$), 141.4 (s, *C*H$_{Py}$), 141.7 (s, *C*H$_{Py}$), 150.7 (s, *C*H$_{Py}$), 151.6 (s, *C*H$_{Py}$), 155.7-155.8 (*C*$_q$), 158.2 (d, $^2J_{P,C}$ = 16.9 Hz, *C*$_q$), 164.3 (d, $^1J_{P,C}$ = 29.6 Hz, *C*=P), 195.7 (d, $^2J_{P,C}$ = 8.1 Hz, *cis*-CO), 204.3 (d, $^2J_{P,C}$ = 31.6 Hz, *trans*-CO); $^{29}$Si NMR (THF-d$^8$) δ = -0.31 (d, $^2J_{P,Si}$ = 8.6 Hz, SiMe$_3$), 4.92 (d, $^2J_{P,Si}$ = 2.7 Hz, SiMe$_3$); $^{31}$P NMR (THF-d$^8$): δ = 264.6 ($^1J_{W,P}$ = 287.7 Hz, $^2J_{P,H}$ = 18.4 Hz).

**Complex 11c: [W(CO)$_4${(Me$_3$Si)$_2$CH}P=C(C$_5$H$_4$N)$_2$}].** $^1$H NMR (THF-d$^8$): δ = 0.28 (s, 18H, SiMe$_3$), 2.80 (d, $^2J_{P,H}$ = 20.0 Hz, $J_{H,H}$ = 14.5 Hz, 1H, C*H*(SiMe$_3$)$_2$), 7.03 (ddt, $^4J_{P,H}$ = 2.8 Hz, $^{3/4}J_{H,H}$ = 5.6 Hz, 1.5 Hz, 1H, C*H*$_{Py}$), 7.12-7.18 (m, 1H, C*H*$_{Py}$), 7.30-7.35 (m, 1H, C*H*$_{Py}$), 7.36-7.39 (m, 1H, C*H*$_{Py}$), 7.62-7.68 (m, 1H, C*H*$_{Py}$), 7.89-7.94 (m, 1H, C*H*$_{Py}$), 8.76 (ddd, $^4J_{P,H}$ = 1.7 Hz, $^{3/4}J_{H,H}$ = 5.2 Hz, 0.8 Hz, 1H, C*H*$_{Py}$), 9.16 (ddd, $^5J_{P,H}$ = 1.7 Hz, $^{3/4}J_{H,H}$ = 5.8 Hz, 0.8 Hz, 1H, C*H*$_{Py}$); $^{13}$C{$^1$H} NMR (THF-d$^8$): δ = 1.8 (d, $^3J_{P,C}$ = 3.6 Hz, SiMe$_3$), 27.2 (d, $^1J_{P,C}$ = 37.9 Hz, *C*H(SiMe$_3$)$_2$), 122.3 (d, $^3J_{P,C}$ = 7.2 Hz, *C*H$_{Py}$), 123.3 (s, *C*H$_{Py}$), 123.5 (s, *C*H$_{Py}$), 126.6 (d, $^3J_{P,C}$ = 7.0 Hz, *C*H$_{Py}$), 137.9 (s, *C*H$_{Py}$), 138.4 (d, $^4J_{P,C}$ = 2.7 Hz, *C*H$_{Py}$), 151.4 (s, *C*H$_{Py}$), 157.5 (d, $^4J_{P,C}$ = 2.1 Hz, *C*H$_{Py}$), 155.5 (d, $^2J_{P,C}$ = 2.7 Hz, *C*$_q$), 157.6 (d, $^2J_{P,C}$ = 8.8 Hz, *C*$_q$), 164.6 (d, $^1J_{P,C}$ = 27.9 Hz, *C*=P), 195.9 (d, $^2J_{P,C}$ = 9.0 Hz, *cis*-CO), 210.3 (d, $^2J_{P,C}$ = 4.7 Hz, *trans*-CO), 212.9 (d, $^2J_{P,C}$ = 39.4 Hz, *trans*-CO); $^{29}$Si NMR (THF-d$^8$) δ = 3.58 (d, $^2J_{P,Si}$ = 5.5 Hz, SiMe$_3$); $^{31}$P NMR (THF-d$^8$): δ = 308.5 ($^1J_{W,P}$ = 274.3 Hz, $^2J_{P,H}$ = 20.0 Hz).

### X-ray crystallographic analyses of 3a, 10c·ZnCl$_2$ and 4e

Suitable single crystals were obtained from concentrated *n*-pentane solutions upon decreasing the temperature from ambient temperature to −20 °C. Data were collected on a Nonius Kappa CCD or a STOE IPDS-2T diffractometer equipped with a low-temperature device at 123(2) K using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Using Olex2[18], the structure was solved with the XS structure solution program using Direct Methods and refined with the XL refinement package using Least Squares minimisation.[19]

Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Centre under the numbers CCDC 1419691 (**3a**), CCDC 1419690 (**4e**), and CCDC 1419692 (**10c**·ZnCl$_2$).

This data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

**Crystal data for 3a.** C$_{23}$H$_{27}$CrN$_2$O$_6$PSi$_2$, M = 566.62, crystal dimensions 0.33 × 0.27 × 0.25 mm$^3$, orthorhombic, space group Fdd2, Z = 16, a = 21.2057(4) Å, b = 52.0922(10) Å, c = 9.9308(2) Å, α = β = γ = 90.00°, V = 10970.1(4) Å$^3$, d$_c$ = 1.372 g mm$^{-3}$, μ = 0.602 mm$^{-1}$, T = 123(2) K, 2θmax = 56°, no. of unique data 6609, R$_{int}$ = 0.0266, R1 (for I>2σ(I)) = 0.0217, wR2 (for all data) = 0.0586, final R = 0.0225, goodness of fit 1.045, ΔF(max/min) = 0.37/−0.29 eÅ$^{-3}$.

**Crystal data for 4e.** C$_{35}$H$_{24}$N$_2$O$_6$PW, M = 783.38, crystal dimensions 0.16 × 0.08 × 0.04 mm$^3$, triclinic, space group P-1, Z = 4, a = 8.8558(2) Å, b = 19.9290(4) Å, c = 19.9303(4) Å, α = 61.0439(8)°, β = 87.8491(8)°, γ = 84.3858(11)°, V = 3062.77(11)Å$^3$, d = 1.699 g cm$^{-3}$, μ = 3.874 mm$^{-1}$, T = 123(2) K, 2θmax = 55.998°, no. of unique data 14790, R$_{int}$ = 0.1177, R1 (for I > 2σ(I)) = 0.0386, wR2 (for all data)= 0.0874, final R = 0.0794, goodness of fit 0.935, ΔF(max/min) = 2.00/−1.87 e Å$^{-3}$.

**Crystal data for 10c·ZnCl$_2$.** C$_{23}$H$_{27}$Cl$_2$N$_2$O$_5$PSi$_2$WZn, M = 818.74, crystal dimensions 0.05 × 0.03 × 0.02 mm$^3$, triclinic, space group P-1, Z = 2, a = 8.7858(8) Å, b = 10.8025(10) Å, c = 17.9022(15) Å, α = 77.250(3)°, β = 86.378(4)°, γ = 66.964(3)°, V = 1524.5(2) Å$^3$, d = 1.784 g cm$^{-3}$, μ = 4.897 mm$^{-1}$, T = 123(2) K, 2θmax = 56°, no. of unique data 7275, R$_{int}$ = 0.0344, R1 (for I > 2σ(I)) = 0.0309, wR2 (for all data) = 0.0672, final R = 0.0423, goodness of fit 1.045, ΔF(max/min) = 1.27/−1.18 e Å$^{-3}$.

### Computational details

All geometry optimizations were run with the ORCA[20] package, using tight convergence criteria and the B3LYP[21] functional together with the def2-TZVP basis set[22] and combined with the latest Grimme's semi-empirical atom-pair-wise London dispersion correction (DFT-D3).[23] The [SD(60,MWB)] effective core potential (ECP) was used for W atoms.[24] Harmonic frequency calculations verified the nature of all computes species having none or one negative (imaginary) frequency for minima or TSs, respectively. Solvent effects (THF) were taken into account via the COSMO solvation model.[25] All properties were computed from the resulting geometries by means of single-point calculations using the more polarized def2-TZVPP basis set.[22] The adiabatic dissociation energy $D_0$ for **4** was computed at the coupled cluster theory level with single-double and perturbative triple excitations (CCSD(T)), using the recently developed near linear scaling domain-based local pair natural orbital (DLPNO) method,[26] using the zero-point energy correction obtained at the optimization level. For the sake of comparison all energy values were also computed with other high level single reference method, such as CEPA (Coupled Electron-Pair Approximation) and in particular the slightly modified NCEPA/1[27] version implemented in ORCA, with the aid of local pair natural orbital (LPNO) schemes.[28] The spin component scaled Møller-Plesset (SCS-MP2) theory[29] and the double-hybrid-meta-GGA functional PWPB95[30] together with the D3 correction were also used. Löwdin charges were obtained from the Löwdin population analysis.[31] Figure 4 was drawn with VMD.[32]

## Conclusions

The synthesis of 3,3-bis(2-pyridyl)oxaphosphirane complexes **3** enabled to discover and study a new intramolecular ring expansion which provided access to complexes having a novel heterobicyclic P-ligand. Apparently, the conditions of the thermally-induced rearrangement is very much dependent on the nature of the P-substituent. DFT calculations on a *P*-Me model derivative of **3** revealed that, despite the easier C-O bond cleavage in oxaphosphirane complex **3**, only the P-C bond cleavage intermediate **6** enables P-N ring closure to give bicyclic complex **4**. Preliminary results on the reaction of complex **3c** with an in situ generated Ti(III) complex offered some insight into the reductively-induced deoxygenation reaction. Although the phosphaalkene complex **10c** was the primary product, it was converted into the *P,N*-chelate complex **11c** and the hetero-dinuclear complex **10c**·$ZnCl_2$.

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