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Two complimentary approaches for the synthesis and isolation of stable phosphanylphosphaalkenes

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Phospha-Wittig (phosphanylphosphinidene titanium(IV) complex) and phospha-Peterson (lithiated diphosphane) reactions were used to obtain phosphanylphosphaalkenes with the general formula XYC=P-P*t*Bu$_2$ (X = alkyl, aryl group or H; Y = alkyl or aryl group). Therefore, two series of reactions with different ketones and aldehydes were performed. An examination revealed that the two methods are complementary. For smaller carbonyl compounds, the phospha-Wittig reaction was shown to be a much better method, while for larger substituents (mainly aromatic), the phospha-Peterson reaction was shown to be a reliable method. These studies led to, among other things, the isolation of seven phosphanylphosphaalkenes in crystalline form after the phospha-Peterson reaction: (Ph)$_2$C=P-P*t*Bu$_2$ (**3a**), *Z*-(Ph)(4-CN-Ph)C=P-P*t*Bu$_2$ (**3c**), (4-CN-Ph)$_2$C=P-P*t*Bu$_2$ (**3d**), (4-MeO-Ph)$_2$C=P-P*t*Bu$_2$ (**3e**), *E*-*t*Bu(Ph)C=P-P*t*Bu$_2$ (**3f**), *E*-{(Me)$_2$N-Ph}(H)C=P-P*t*Bu$_2$ (**4d**) and *E*-PhPh(H)C=P-P*t*Bu$_2$ (**4e**). Corresponding compounds were obtained at high yields under mild conditions, and more importantly, these new species are relatively air- and absolutely moisture-stable, especially these originating from aldehydes. Additionally, a comprehensive DFT study helped us to establish not only the key factors crucial for the effective phospha-Wittig-based synthesis of C=P-P species but also the consecutive steps along the reaction path leading to the formation of these compounds.

Introduction

Phosphorus compounds displaying low coordination numbers and multiple bonds resemble related carbon compounds and show considerable reactivity.[1, 2] The P=C bond is polarized with the P atom as the positive pole, but some substituents, especially NR$_2$ groups at the carbon atom of the P=C moiety, can lead to reverse polarization.[3, 4] The HOMO-LUMO separation is smaller in phosphaalkenes than in alkenes.[5] Generally, the P=C group in R~P=CR^{1}R^2 is more reactive[2] than the C=C group in R^{1}R^{2}C=CR^{3}R^4. Unprotected phosphaalkenes are very reactive transient species with rather no good prospects for applications.[6] Since the first synthesis reported by Becker,[7] the synthesis of phosphaalkenes has been intensively studied, several methods and have been reported (Figure 1), including the phospha-Wittig and phospha-Peterson reactions.[8-20]

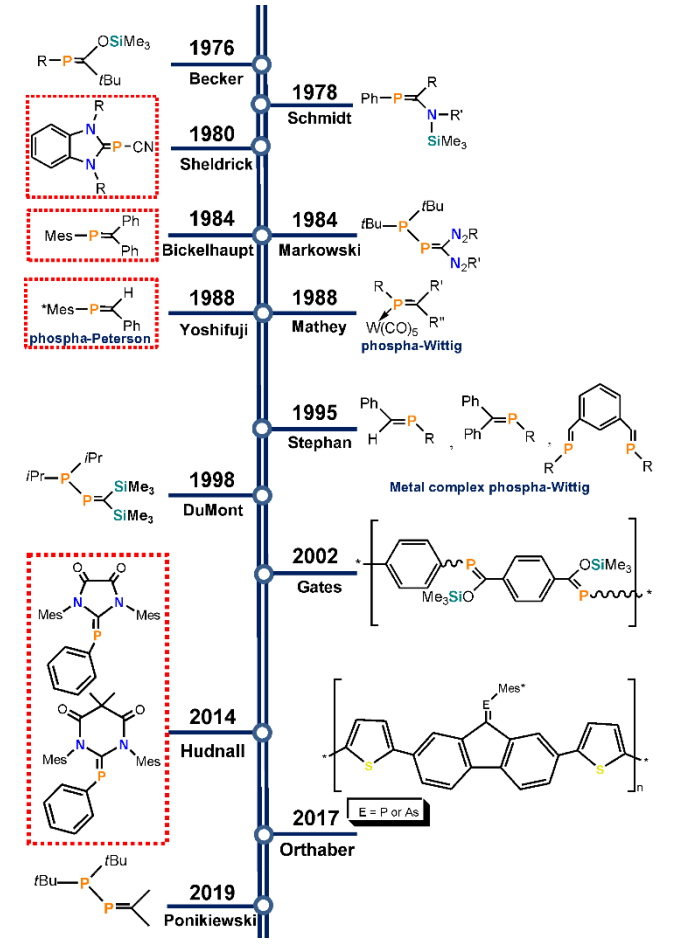

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Figure 1. Selected contributions on phosphaalkenes and phosphanylphosphaalkenes. The red boxes indicate compounds obtained in crystalline form.

Recently, materials for new functional polymers and copolymers have received attention. The Gates group studied polymerization reactions, especially that of MesP=CPh$_2$. This monomer is isolable and sufficiently reactive, so it was possible to polymerize this compound with anionic[7,21-23] cationic[24] and radical[25, 26] initiators. The addition of free radicals to MesP=CMe$_2$ using the muonium analog of hydrogen was recently studied.[27] This group also studied polycondensation reaction similar to Becker's[7] silatropic reaction, leading to π-conjugated polymers containing P=C bonds.[28] Protasiewicz *et al* studied the synthesis and properties of phospha-PPV oligomers with P=P and P=C functionalities.[29-31] The phosphaalkene moiety Mes*P=C (Mes* = 2,4,6-*t*Bu$_3$C$_6$H$_2$) can also be incorporated into butadiyne-expanded dendralene fragments.[32] The serious barriers to the use of diverse phosphaalkenes as monomers for polymerization or copolymerization are a lack of suitable synthesis methods and difficulties in matching their reactivity. Generally, the proper monomer must be sufficiently stable but still reactive. The stabilization of the P=C functional group in phosphaalkenes can be accomplished in two ways. The first method is thermodynamic stabilization by incorporating the P=C bonds into a delocalized p_π-p_π system or incorporating substituents that enhance the positive charge at the P atom, e.g., the stability of phosphabenzene C_5H_5P,[5] Me_3Si-C≡C–P=C(SiMe$_3$)$_2$,[33] HP=C(NR$_2$)F,[34] and F$_3$CP=C(OR')NR$_2$[35] and the moderate stability of F$_3$CP=C(F)NR$_2$.[36] The structural outcomes of these conjugations are strongly dependent on the site of attachment (C *vs*. P) and on the character of all substituents.[37] The second stabilization method, kinetic stabilization, uses bulky substituents. The very bulky Mes* moiety on the P atom in Mes*P=CR^{1}R^2 results in high stability (low reactivity) of phosphaalkene regardless of the nature of the R^1 and R^2 groups, e.g., the high stability of Mes*P=CH$_2$.[38, 39] The steric protection offered by Mes (2,4,6-Me$_3$C$_6$H$_2$) is smaller, and MesP=CPh$_2$ was the monomer of choice in the polymerization studies.[25-27] Importantly, there are several compounds of the type R^{1}R^{2}P-P=CR^{3}R^4 that mainly include silyl substituents on the carbon atoms. Phosphanylphosphaalkene with the formula *i*Pr$_2$P-P=C(SiMe$_3$)$_2$, was subjected to a Diels-Alder reaction and was oxidized with S and Se.[15] Compounds with the general formula *t*Bu$_2$P-P=C(NR$_2$)(NR$^1_2$) have been reported, and the ^{31}P and ^{13}C NMR spectra of these compounds revealed the reverse polarity induced by the R$_2$N groups, which are strong π-donors, in the β-position to the λ^{3}σ^4-P-atom.[40]

Recently, we proved that phosphanylphosphido complexes of Ti(III) are good reagents in the phospha-Wittig reaction, yielding an intermediate that leads directly to the phosphanylphosphaalkene, representing the phosphorus extension of the compounds described above. It has long been known that the phosphinidene complexes of early transition metals and lanthanides, e.g., Sc(III),[41] Ti(IV),[42, 43] Zr(IV),[16, 44] Ta(V),[45] and Lu(III),[46] are powerful phospha-Wittig reagents due to the high oxo- and halogenophilicity of these metal centers. Herein, we report two different methods of synthesis of phosphanylphosphaalkenes. The first uses the metal-phospha-Wittig reagent titanium(IV) complex [(BDI*)Ti(Cl){η^2-P-P*t*Bu$_2$}],[47] (BDI* = 2,6-diisopropylphenyl-β-methyldiketiminate ligand) which is a powerful transfer vehicle of the phosphanylphosphinidene *t*Bu$_2$P=P in reactions with aldehydes and ketones. The second is a modification of Petersen phospholefination using reactions of *t*Bu$_2$P-P(SiMe$_3$)Li[48, 49] with aldehydes and ketones. We compare the scope and limitations of these two methods.

Results and discussion

At the beginning of our research, we only knew that reactions of β-diketiminate titanium(III) complex containing phosphanylphosphido ligand with acetone, acetophenone, cyclopentanone, cyclohexanone and 9-fluorenone lead to new compounds with a C=P-P bond system, namely, phosphanylphosphaalkenes.[50, 51] Our studies allowed us to isolate few phosphanylphosphaalkenes in oily form, but the isolation of phosphanylphosphaalkenes with aromatic groups on the central carbon atom remained challenging. By selecting a titanium complex as a starting material for earlier research, we were able to control the nucleophilicity of the phosphorus atom in the titanium complex.[52] The more nucleophilic the phosphorus atom is, the more likely it is that the reaction will be successful. Nucleophilic phosphinidene metal complexes were previously used successfully for the transfer of PR groups.[16, 46] The nucleophilic properties of the $P_{phosphido}$ in the [(BDI*)Ti(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] were poor (calculated value of the nucleophilic condensed Fukui function f_N = 0.043); however, despite these poor properties, the reaction with ketones occurred. The identification of the electrophilic and nucleophilic centers in the β-diketiminate titanium(IV) complex with the phosphanylphosphinidene ligand [(BDI*)Ti(Cl){η^2-P-P*t*Bu$_2$}] (**1**) revealed that the $P_{phosphinidene}$ atom is the most nucleophilic site in the structure (f_N is 0.241). Thus, **1** is expected to be a better material for reactivity investigation with aldehydes and ketones in the phospha-Wittig reaction. Additionally, the use of the titanium(IV) complex could eliminate the side reactions we observed, namely, aldol condensation and pinacol condensation. This should facilitate the isolation as well as increasing the yields of the desire final products which are phosphanylphosphaalkenes. Our goal was to optimize the reaction for phosphanylphosphaalkenes formation.

Phospha-Wittig reaction of [(BDI*)Ti(Cl){η^2-P-PtBu$_2$}] (1) with ketones and aldehydes

We conducted a series of reactions of [(BDI*)Ti(Cl){η^2-P-P*t*Bu$_2$}] (**1**) with selected ketones and aldehydes in THF in a 1:1 molar ratio, as shown in Scheme 1.

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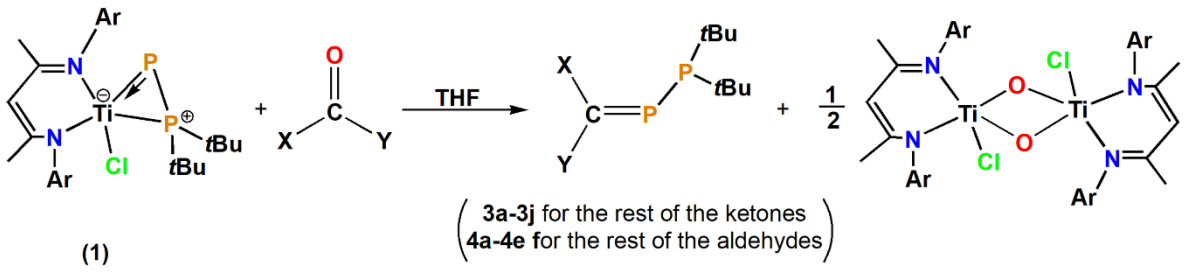


Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

3a: X = Y = Ph;
3b: 9-fluorenone
3c: X = Ph, Y = 4-CN-Ph;
3d: X = Y = 4-CN-Ph;
3e: X = Y = 4-MeO-Ph;
3f: X = Ph, Y = *t*Bu;
3g: X = Y = Me;
3h: cyclohexyl ring;
3i: X = Ph, Y = Me;
3j: X = Me, Y = cyclopropyl ring;
4a: X = H, Y = *i*Pr;
4b: X = H, Y = cyclohexyl ring;
4c: X = H, Y = 4-Me-Ph;
4d: X = H, Y = 4-(Me$_2$N)-Ph;
4e: X = H, Y = 4-Ph-Ph;

Scheme 1. Reactions of **1** with a suitable ketone or aldehyde in THF.

In each case, to the green solution of **1,** a suitable ketone or aldehyde was added dropwise. The reaction time was different and depended on the ketones used, whereas all selected aldehydes reacted within the same time (after 24 hours, the reaction was finished). Generally, **1** reacts with aromatic ketones very slowly; for example, the reaction with benzophenone leading to the formation of (Ph)$_2$C=P-*t*Bu$_2$ (**3a**)[50] was complete after 3 months (the signals attributed to **1** in the ^{31}P{^{1}H} NMR spectrum were not observed, see ESI Figure S1). Importantly, taking into account the reactions of the complexes of titanium(III) and titanium(IV), using this with a phosphanylphosphinidene ligand limits the reaction byproducts and simplifies the entire process. The application of titanium(IV) complex **1** prevents the formation of undesirable products (aldol and pinacol condensation) and yields only phosphanylphosphaalkenes and dimeric Ti(IV) complex [(BDI*)Ti(Cl)(μ_2-O)]$_2$, as reported in the literature.[53] Additionally, we found that the effect of the substituent (-CN or OMe$_3$) in the *para* position of the aromatic rings in the selected ketones does not increase the reactivity, while ketones such as 4-cyanbenzophenone, 4,4'-dicyanbenzophenone and 4,4'-dimethoxybenzophenone slow the reaction even more. The ^{31}P{^{1}H} NMR spectra obtained after three months revealed the presence of the starting Ti(IV) complex with the phosphanylphosphinidene ligand (d, 843.47 ppm, 143.57 ppm, J_{P-P} = 450.5 Hz),[47] and in the ^{1}H NMR spectrum, the signals from the unreacted ketones were also visible (see ESI Figure S3-S5). Additionally, we calculated the values of the electrophilic condensed Fukui functions (f_E) for the carbonyl carbon atom and the nucleophilic condensed Fukui functions (f_N) for the carbonyl oxygen atom of the ketones and evaluated the dependence of the rate of reactions. The results indicated some differences in f_E, which ranged from 0.101 (4-cyanbenzophenone) to 0.192 (cyclopropyl methyl ketone), and in f_N – from 0.139 (4,4'-dimethoxybenzophenone) to 0.386 (acetone). The obtained results revealed that the high nucleophilicity of oxygen atom together with a steric hindrance rather than electrophilicity of carbonyl carbon atom accounts for its reactivity towards **1 (**see ESI, Table S7**)**. In general, the more nucleophilic the oxygen atom of reacting ketone, and the less steric bulk of **X** and **Y** substituents in X-C(=O)Y, the faster the reaction. The calculations of the Fukui functions also showed small influence of activating or deactivating substituents on the aromatic ring of the ketones on the course of the reaction; comparing reactions involving benzophenone and its substituted counterparts (**3a**, **3c**, **3d** and **3e**), all species slowly reacts with **1** (with similar values of the carbon f_E and the oxygen f_N). Presence of either electron-donating (-OMe in **3e**) or electron-withdrawing (-CN in **3c** and **3d**) slows down the reaction, presumably because of increasing bulkiness of substituents in relation to non-substituted **3a**. Hence, we assume that steric rather than electronic properties of aromatic ring substituents influence the kinetic of reaction (see Figure 2 for energy barriers of these reactions): OMe substituent is the most sterically demanding, and therefore, formation of **3e** is the slowest one (in relation to **3a**, **3c** and **3d**). However, aromatic substituents do not preclude the fast conversion into the respective C=P-P system. A more rational explanation of these obtained is the steric hindrance of ketones and the facile formation of the potential intermediate titanium complex. This assumption was confirmed by the reaction of **1** with *tert*-butyl phenyl ketone (f_E = 0.121 of C and f_N = 0.295 of O). The ^{31}P{^{1}H} NMR spectrum of the reaction mixture after three months shows only signals attributed to starting **1** (839.89 ppm and 142.05 ppm, J_{P-P} = 450.5 Hz),[47] while signals attributed to the phosphanylphosphaalkene *t*Bu(Ph)C=P-P*t*Bu$_2$ (**3f**) were not

visible (see ESI Figure S6). The above-described problems (long reaction times or no reaction) were not observed for the reactions of **1** with aliphatic ketones, acetophenone and aldehydes, which were completed after 24 hours. In all cases, phosphanylphosphaalkenes were formed as the main products. Thus, we obtained phosphanylphosphaalkenes very easily in the reaction with acetone, cyclohexanone and acetophenone, as previously described by us: $(Me)_2C$=P-P*t*Bu_2 (**3g**), $(CH_2)_5C$=P-P*t*Bu_2 (**3h**), and (Me)(Ph)C=P-P*t*Bu_2 (**3i**).[50, 51] In the reaction of **1** with cyclopropyl methyl ketone, we obtained a new phosphanylphosphaalkene with the formula $(CH_2CH_2CH)(Me)C$=P-P*t*Bu_2 (**3j**). In the reaction of **1** with aldehydes in each case, we also obtained new phosphanylphosphaalkenes: {$(Me)_2CH$}(H)C=P-P*t*Bu_2 (**4a**), {$(CH_2)_4CH$}(H)C=P-P*t*Bu_2 (**4b**), (*p*-Me-Ph)(H)C=P-P*t*Bu_2 (**4c**), {$(Me)_2N$-Ph}(H)C=**P**-P*t*Bu_2 (**4d**), and PhPh(H)C=**P**-P*t*Bu_2 (**4e**). The $^{31}P\{^1H\}$ NMR shifts of the formed phosphanylphosphaalkene (calculated and experimental) are listed in Table S3 in ESI. It should also be mentioned that among the obtained phosphanylphosphaalkenes, compounds **3g**, **3h**, **3i**, **3j, 4a, 4b,** and **4c** were isolated in pure form using a distillation process. Unfortunately, phosphanylphosphaalkenes **3a**, **3b**, **3c**, **3d**, **3e, 4d,** and **4e** were not isolated. The boiling points of these phosphanylphosphaalkenes were too high, up to 200°C, and we did not observe any fraction. However, above this temperature, we observed decomposition of the dimeric complex $[(BDI^*)Ti(Cl)(\mu_2\text{-}O)]_2$ and migration of the BDI*H ligand. On the other hand, the crystallization process of $[(BDI^*)Ti(Cl)(\mu_2\text{-}O)]_2$ was not complete, and even after several crystallization processes, we still observed typical signals of the $[(BDI^*)Ti(Cl)(\mu_2\text{-}O)]_2$ in the ^1H NMR spectrum.[53] Due to problems with isolation, it can be concluded that this method is not suitable for obtaining phosphanylphosphaalkenes with aromatic groups.

Asymmetric ketones reacted with **1** and yielded two isomers each time (for **3c**, **3i**, and **3j)**. In **3c**, the percentage ratio of the *Z* and *E* isomers in the reaction solution was 66% : 34%. In the reaction mixture of **1** with acetophenone, the *E* isomer constituted approximately 90%, while the isolation temperature (160°C) caused changes in the ratio: the amount of *E* isomer was reduced (60%), and that of the *Z* isomer (40%) was increased. In the reaction of **1** with cyclopropyl methyl ketone, we did not observe large differences in the percentage ratio of isomers between the reaction mixture (*Z* : *E* 55% : 45%) and the isolated products (*Z* : *E* 53% : 47%). In the reaction of **1** with aldehydes, the formation process of phosphanylphosphaalkenes was substantially stereoselective. In all reactions, the amount of the *E* isomer was 100%, and only in the reaction with isobutyraldehyde and cyclohexacarboxyaldehyde was the percentage amount of the *E* isomer slightly smaller: 97% and 93% (all NMR spectra after reaction of **1** with aldehydes see ESI Figure S19-S47). Notably, the isolation of phosphanylphosphaalkenes by the distillation process ({$(Me)_2CH$}(H)C=P-P*t*Bu_2 (**4a**), {$(CH_2)_4CH$}(H)C=P-P*t*Bu_2 (**4b**), (p-Me-Ph)(H)C=P-P*t*Bu_2 (**4c**)) had no effect on the percentage ratio of the isomers. The formation of only the *E* isomer (or the significant predominance of this isomer) may be the result of steric hindrance of the final phosphanylphosphaalkene and steric hindrance of the intermediate titanium complex. The formation of the *E* isomer of the phosphaalkene was previously observed by Protasiewicz and Ott.[54, 55] Protasiewicz and coworkers described the formation of a mixture of *E* and *Z* isomers by exposure of the compound $(2,6\text{-}Mes_2C_6H_3)P$=C(H)(Ph) to UV light.[55] Interestingly, the influence of UV light (room light or a UV lamp) on phosphanylphosphaalkenes was not observed in our work.

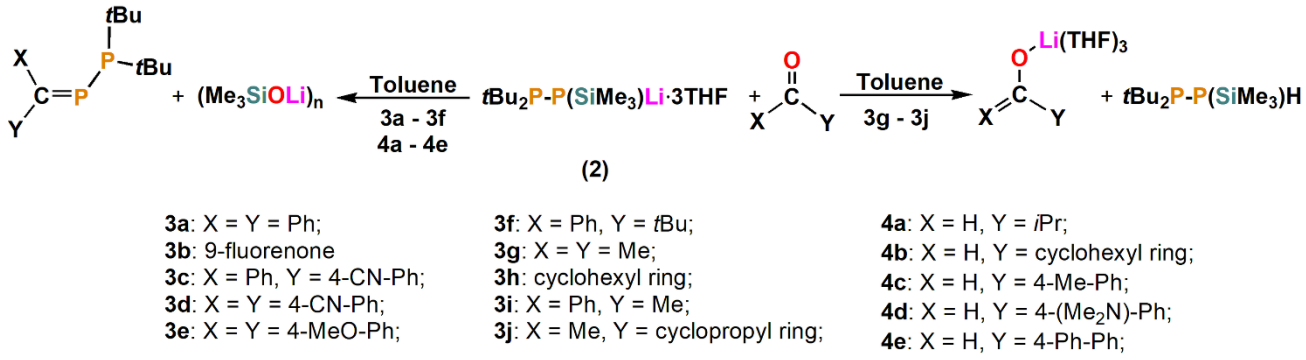
In summary, the β-diketiminate titanium(IV) complex with a phosphanylphosphinidene ligand is an appropriate reactant in the phospha-Wittig reaction. In all reactions, the expected phosphanylphosphaalkenes were obtained and characterized by NMR spectroscopy (except the reaction with *tert*-butyl phenyl ketone). The only problem was the isolation process of pure phosphanylphosphaalkenes with aromatic rings on the carbon atom.

Phospha-Peterson reaction of *t*Bu_2P-P(SiMe3)Li (2) with ketones and aldehydes

In our search for a method that would allow the isolation of some phosphanylphosphaalkenes, particularly those containing aromatic groups, we decided to use the phospha-Peterson reaction. The method of phosphaalkene synthesis reported by Gates and coworkers was successfully used.[56] In our syntheses, we used the lithium salt of diphosphane with the formula *t*Bu_2P-P($SiMe_3$)Li·3THF (**2**) containing a P-P bond and selected ketones or aldehydes. In each case, we dripped the carbonyl compound or its solution into a solution of lithium salt of diphosphane. In contrast to the reaction of the β-diketiminate titanium(IV) complex with a phosphanylphosphinidene ligand, this method allowed us to isolate phosphanylphosphaalkenes containing aromatic substituents in crystalline form in reactions with the following ketones: benzophenone, 4-cyanbenzophenone, 4,4'-dicyanbenzophenone, and 4,4'-dimethoxybenzophenone. This method also contributed to the isolation of the product of the reaction with *tert*-butyl phenyl ketone. As a result, we isolated and characterized five new compounds: $(Ph)_2C$=P-P*t*Bu_2 (**3a**), *E*/*Z*-(Ph)(4-CN-Ph)C=P-P*t*Bu_2 (**3c**), $(4\text{-}CN\text{-}Ph)_2C$=P-P*t*$Bu_2$ (**3d**), $(4\text{-}MeO\text{-}Ph)_2C$=P-P*t*$Bu_2$ (**3e**), and *t*Bu(Ph)C=P-P*t*Bu_2 (**3f**). The NMR spectra (^1H, ^{31}P, ^{13}C) of the isolated compounds confirmed the purity of the obtained products. In the case of compound **3c**, we observed signals from two isomers in the $^{31}P\{^1H\}$ NMR spectrum (see ESI Figure S62). Integration of the ^1H NMR spectrum revealed that the *Z* isomer constituted 72%, while the *E* isomer constituted 38%. Interestingly, the X-ray analysis revealed only the *Z* form in the crystalline product, but the crystals dissolved in C_6D_6 show signals from both the *E* and *Z* isomers (*E*-to-*Z* ratio: 8% to 92%). A similar composition of isomers in the crystalline product and in solution was observed by Gates and coworkers for the following phosphaalkenes: MesP=C(Ph)(4-$OMeC_6H_4$) and MesP=C(Ph)(2-py).[56] The reaction with *tert*-butyl phenyl ketone yielded the corresponding phosphanylphosphaalkene as a yellow oil. Analysis of the $^{31}P\{^1H\}$ NMR data indicated the formation of mainly one isomer of the expected phosphanylphosphaalkene (Z = 98%).

A different situation was noticed in the case of the reactions of **2** with aliphatic ketones and acetophenone. The first difference was a very slight change in the reaction color (rather pale yellow). The $^{31}P\{^{1}H\}$ NMR spectra of the reaction mixtures revealed mainly the presence of diphosphane *t*Bu$_2$P-P(SiMe$_3$)H (19.07 ppm, (d), -197.30 ppm, (d), J_{P-P} = 190.5 Hz) and very small signals (or a complete absence of signals) attributed to phosphanylphosphaalkenes. The presence of diphosphane was previously observed by us in the reaction of a β-diketiminate titanium(III) complex with a phosphanylphosphido ligand, e.g., with acetone, acetophenone, and cyclohexanone, and it was related to the aldol condensation process.[50, 51] Interestingly, spectroscopic investigations of the reaction mixture of **2** with cyclopropyl methyl ketone did not reveal the aldol condensation product. In the ^{1}H NMR spectrum, signals attributed to one cyclopropyl group were observed (2.13 ppm ^{1}H and 0.79 ppm, 0.55 ppm, 4H). Additionally, in the range of 3.79 ppm, a broad singlet was observed, which is correlated with the carbon atom at 80.48 ppm in the $^{13}C\{^{1}H\}$ spectrum. The integration of the ^{1}H spectrum revealed that the cyclopropyl, vinyl and THF protons are correlated with each other. In effect, this finding may indicate the formation of the (CH$_2$CH$_2$CH)(CH$_2$=)C-OLi(THF)$_3$ compound. Additionally, the integrations of all protons in the ^{1}H NMR spectrum revealed that the formations of both compounds, (CH$_2$CH$_2$CH)(CH$_2$=)C-OLi(THF)$_3$ and *t*Bu$_2$P-P(SiMe$_3$)H, are related to each other (see Scheme 2, all NMR spectra of reaction mixture of 2 with cyclopropyl methyl ketone see Figure S108-S113). Enolate lithium salts were also formed in the reactions with acetophenone and cyclopentanone (all NMR spectra of reaction mixture of 2 with acetophenone and cyclopentanone see Figure S97-S107). In the case of reaction with acetone, we also observed in the $^{31}P\{^{1}H\}$ NMR spectrum the signals associated with formation of diphosphane *t*Bu$_2$P-P(SiMe$_3$)H (19.07 ppm, -197.30 ppm, J_{P-P} = 187.7 Hz) and enolate lithium salt ($^{13}C\{^{1}H\}$-DEPT 135: 81.82 ppm). Unlike the other reactions where enolates are formed, in this reaction the lithium salt of diphosphane ($^{31}P\{^{1}H\}$ NMR: 46.57 ppm, -245.14 ppm, J_{P-P} = 278.4 Hz)[49] and acetone (^{1}H NMR: 1.86 ppm) are present in the reaction mixture (all NMR spectra of reaction mixture of 2 with acetone see Figure S91-S96). The obtained result may suggest that in this reaction an equilibrium is established between the reaction products and the reactants. To confirm this assumption, we calculated value of the free energy of the reaction ΔG_{298K} and related equilibrium constant K_{298K} by applying DFT methods. The obtained thermodynamic parameters justify presence of unreacted substrates in the reaction mixture. The equilibrium constant K_{298K} of 5.1 (ΔG_{298K} = -4.03 kJ mol^{-1}) is responsible for an 83.6% conversion degree of substrates to products (see ESI, Table S4).

The reactions of the lithium salt of diphosphane (**2**) with aldehydes occurred analogously to those with aromatic ketones and were finished after 24 hours. Each of these reactions yielded a phosphanylphosphaalkene as the main product. Compounds **4d** and **4e** were isolated in crystalline form, while **4a**, **4b** and **4c** were obtained as oils. After each reaction leading to the phosphanylphosphaalkenes, we isolated a compound composed of [LiOSiMe$_3$]$_8$ moieties from the reaction solution (see ESI Figure S154). Analogically compounds with Li$_8$O$_8$ core but with different organic ligand were found in the literature: [LiO*t*Bu]$_8$ and [LiOCH$_2$*t*Bu]$_8$.[57, 58] Additionally, in the literature are also known lithium compounds stabilized with OSiMe$_3$ groups, an example of which is [Li$_7$(OSiMe$_3$)$_7$(THF)].[59]



Scheme 2. Reactions of **2** with a suitable ketone or aldehyde in toluene.

In summary, the second method of phosphanylphosphaalkene synthesis has many advantages. Most importantly, this method is much simpler and eliminates the synthesis of the titanium(IV) complex with a phosphanylphosphinidene ligand. Furthermore, the isolation of the obtained phosphanylphosphaalkenes is much easier (the distillation process is eliminated). This method facilitates the preparation of phosphanylphosphaalkenes with aromatic groups. Unfortunately, simultaneous use is not suitable for compounds with aliphatic groups (presence of the α proton). In these cases, the reaction led to diphosphane and to the lithiated enol form of the ketones.

Stability investigations

The first sign that the obtained and isolated compounds could be stable was the lack of formation of [2+2] cyclodimerization products. Earlier, in the literature, both Ott and Gates described the two routes of dimerization process of phosphaalkenes (head-to-head and head-to-tail) and molecular structure of the dimer.[56, 60, 61]

Likewise, the newly obtained compounds seem attractive for further reactivity studies; therefore, we decided to test the stability of the phosphanylphosphaalkenes isolated in crystalline form under air and water conditions. Interestingly, all

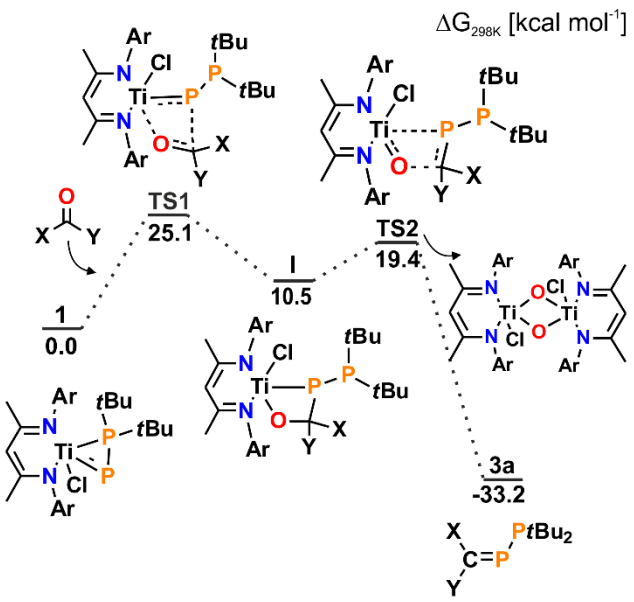
phosphanylphosphaalkenes are very stable in the water, for example the water (2:1 ratio) was added to the Ph_2C=P-P*t*Bu_2 (**3a**) and then the reaction mixture was observed spectroscopically for 2 weeks (see ESI Figure S133) and any changes were noticed.

Additionally, we exposed compounds **3a**, **3c**, **3d**, **3e**, **4c**, and **4d** to air (RT), and we observed how the color of the crystals changed. We observed that all phosphanylphosphaalkenes obtained after reactions with ketones (**3a**, **3c**, **3d**, **3e**) are stable for about two weeks, while the phosphanylphosphaalkenes obtained after reactions with aldehydes (**4d** and **4e**) are permanently stable under air conditions (see ESI, Figure S149-S150). Furthermore, we also checked to which compounds the phosphanylphosphaalkenes **3a**, **3c**, **3d**, **3e** decompose. Therefore, we dissolved one of the phosphanylphosphaalkenes (**3a**) in C_6D_6, and then we recorded the NMR spectra ($^{31}P\{^1H\}$ and $^1H\}$) every few days until the compound was completely decomposed (the NMR tube was not under an argon atmosphere). After 5 days, the $^{31}P\{^1H\}$ NMR spectrum showed signals of the phosphanylphosphaalkene (d, 277.32 ppm, 27.39 ppm, J_{PP} = 228.9 Hz), which indicates that 3a is still stable in the solution. New signals appeared after 7 days (two singlets, 66.00 ppm and 33.51 ppm), and after 2 weeks, the new signals increased in intensity, while the signals from phosphanylphosphaalkene disappeared. After the same time (2 weeks), the orange crystals of **3a** became colorless. The ^{31}P NMR spectrum showed a doublet of multiplets at 66.01 ppm (J_{PH} = 441.7 Hz), whereas at 33.51 ppm, a doublet of doublets was observed (J_{PH} = 560.2 Hz, J_{PH} = 19.4 Hz). The $^{31}P\{^1H\}/^1H$ spectrum revealed a correlation of the phosphorus signals at 66.0 ppm with two doublets: at 5.65 ppm (J_{PH} = 441.7 Hz) and at 0.83 ppm (J_{PH} = 15.3 Hz). The obtained NMR results suggest decomposition leading to the *t*Bu_2PH(=O) product, which was confirmed by literature data.[62] Further analysis revealed a correlation between the phosphorus atom at 33.51 ppm and the aromatic protons at 7.31 ppm, with a doublet at 6.91 ppm (J_{PH} = 560.2 Hz) and a doublet at 4.09 ppm (J_{PH} = 19.4 Hz). Additionally, in the $^{13}C\{^1H\}/^1H$ spectrum, the proton at 4.09 ppm is correlated with the carbon atom at 53.35 ppm (d, J_{PC} = 90.46 Hz). The obtained results indicate that the carbon atom in the C=P moiety is now protonated and that a single bond now exists between the carbon and phosphorus atoms. Similar shifts of the protons, carbon atoms and coupling constants discussed above were observed for [3,6-bis(dimethylamino)-9*H*-xanthen-9-yl]phosphinic acid.[63] Furthermore, in the ^1H NMR spectrum, the typical broad singlet of the OH group was also observed (11.91 ppm). The obtained results suggest the formation of Ph_2(H)C-PH(=O)(OH) as the second compound in the decomposition process.

The $^{31}P\{^1H\}$ NMR spectra obtained after decomposition process of **3c**, **3d** and **3e** revealed the same two singlets at 66.00 ppm and 33.51 ppm (all stability and decomposition spectra see ESI Figure S142-S147).

DFT Calculations

Unlike its reactivity towards aldehydes, the reactivity of **1** towards ketones differs depending on the steric and electronic properties of the substituents bound to the C=O atom. Hence, to elucidate why the diversity of ketones affects the reaction progress and how (by influencing the kinetic and/or thermodynamic parameters), we decided to study the reaction mechanism by applying DFT methods. According to relaxed scans of the potential energy surface in each case, the reaction proceeds through a two-step mechanism: complexation of the respective ketone to starting **1** and subsequent decomposition of the obtained complex into final products **3a**-**3j** and the dimeric byproduct $[(BDI^*)Ti(Cl)(\mu_2\text{-}O)]_2$ (Figure 2). The established reaction mechanism involving two-step transformation is in accord with the literature data and our own experience gained while studying the reaction of Ti(III) complexes containing a phosphanylphosphido ligand with ketones.[16, 50, 51, 64] The reaction starts with the simultaneous formation of Ti-O and P-C bonds via the four-membered-ring transition state $\mathbf{TS_1}$(**3a**-**3j**) to give intermediate **I**(**3a**-**3j**). In the next step, the splitting of both the C-O bond of the carbonyl group and the P-Ti bond (if still present) along with the formation of C=P double bond leads to final phosphanylphosphaalkenes **3a**-**3j**. In general, the more nucleophilic the O atom and the less electrophilic the C atom in the C=O group, the more thermodynamically privileged is the formation of **I** and the lower is the overall energy barrier of the reaction (Figure 2; see ESI, Table S6). Despite the electronic effects, bulky substituents slightly disturb the established order of reactivity, facilitating reactions with small ketones. Hence, both the electronic and steric properties of the reacting carbonyls account for the overall kinetics of the reaction. This justifies why **3b**, **3h** and **3i** are associated with the lowest energy barriers – the respective ketones satisfy both these conditions. The formation of **3g** and **3j** proceeds slightly more slowly – CH3C(O)CH3 and c-PrC(O)Me bear small substituents; however, these compounds are less electronically privileged due to the high electrophilicity of **C**=O. The reactions involving bulky ketones to give **3a**, **3c**, **3d**, and **3e** are much slower, with a maximum energy barrier for **3f,** the reaction of which does not occur even if mixing is maintained over 3 months. All transformations are energetically favored, with significantly negative values of ΔG^o_{298} ranging between -27.2 kcal mol^{-1} and -37.2 kcal mol^{-1}. Hence, kinetic rather than thermodynamic parameters limit the scope of ketones that may be transformed to the respective C=P-P products via this method.



3b:	21.7	-7.4	17.2	-36.1
***Z*-3c:**	25.5	8.9	17.3	-37.2
***E*-3c:**	25.7	5.8	17.0	-34.5
3d:	25.0	3.8	15.2	-36.1
3e:	25.7	13.0	21.6	-32.7
***Z*-3f:**	28.1	7.1	22.1	-31.3
***E*-3f:**	29.6	5.5	28.7	-25.5
3g:	24.2	4.1	16.7	-28.0
3h:	20.0	-1.2	12.5	-31.8
***Z*-3i:**	24.5	3.9	17.5	-29.0
***E*-3i:**	21.9	-2.1	20.1	-30.1
***Z*-3j:**	22.9	6.0	18.3	-27.8
***E*-3j:**	23.4	9.3	20.2	-27.2

Figure 2. A Gibbs free energy profile of formation of **3a-3j** calculated at TPSSTPSS//6-31+G(d,p) (TPSSTPSS//LANL2DZ for Ti) level of theory. The energy values for the formation of **3a** were presented on the diagram.

Considering reactions with unsymmetrical ketones (**3c**, **3i** and **3j**), the *E*/*Z* isomer ratio may be justified based on calculated energy barriers and values of free energies associated with each transformation (Figure 2). In the case of **Z-3c** and **Z-3j**, the *Z* isomers form not only faster**,** but also they are more energetically favored products than the corresponding *E* isomers, explaining their high content in the reaction mixture. Conversely, the formation of ***Z*-3i** is neither kinetically nor thermodynamically favored, which accounts for its low content in the reaction mixture.

The UV-VIS spectra conducted for the isolated in solid form phosphanylphosphaalkenes (**3a**, **3c**, **3d**, **3e**, **3f**, **4c** and **4d**) revealed two absorption band assigned to the π-π* and n-π* transitions (Figure 3, see ESI Table S8). The UV-VIS spectrum of **3a** (no substituents in the aromatic rings) shows intensive absorption band for the π-π* transition in the short wavelength (322 nm) and very weak absorption band for the n-π* transition in the longest wavelength (440 nm). In comparison, the absorption bands found in the literature for phosphaalkenes (π-π* transition) are respective: (MesP=C(Ph)(1-naphthyl) 298 nm, MesP=C(Ph)(9-phenanthryl) 302 nm, MesP=P(Ph)(5-dibenzosuberenyl) 294 nm and MesP=C(Ph)(Pyr) 390 nm.[65, 66] Different substituents in the para position cause bathochromic shifts of the absorption band into longer wavelengths (compared with the spectra of **3a**). The same dependences were observed for the phosphaalkene substituted in the para position (-OMe or NMe_2 groups).[67] Importantly, the very weak absorption bands assigned to the n-π* transition are additionally often overlapped by the π-π* transition absorption bands, therefore they are confirmed by the theoretical UV-VIS spectra performed for phosphanylphosphaalkenes **3a**, **3c**, **3d**, **3e**, **3f**, **4c** and **4d** (see ESI, Figure S236-S249).

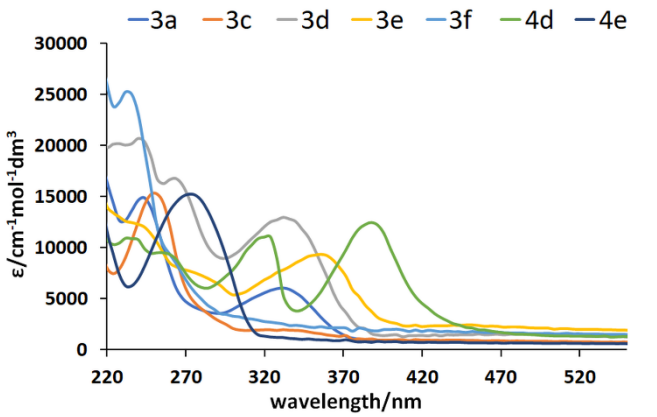


Figure 3. UV-vis spectra of **3a**, **3c**, **3d**, **3e**, **3f**, **4d** and **4e** in a 3 x 10^{-5} M n-pentane solution.

X-ray structural analysis

All crystals of phosphanylphosphaalkenes were obtained only in the phospha-Peterson reaction. Selecting the appropriate solvents and crystallization conditions enabled us to obtain good-quality crystals for X-ray crystallography (for details, see ESI, Experimental Section). Compounds **3a**, **3d**, and **3e** crystallize in the monoclinic space groups *C*2/*c* (**3a**), $P2_1/c$ (**3d**) and $P2_1/n$ (**3e**), whereas **3c** crystallizes in the orthorhombic space group *Pbcn*. In the independent part of the unit cell, only one molecule of phosphanylphosphaalkene existed for **3a**, **3c**, and **3e**; only for compound **3d** were two molecules present. The molecular structures of **3a** and **3c** are shown in Figure 4. (For the molecular structures of **3d** and **3e**, see ESI Figures S151 and S152; for measurement details, see ESI, Table S1 and S2.).

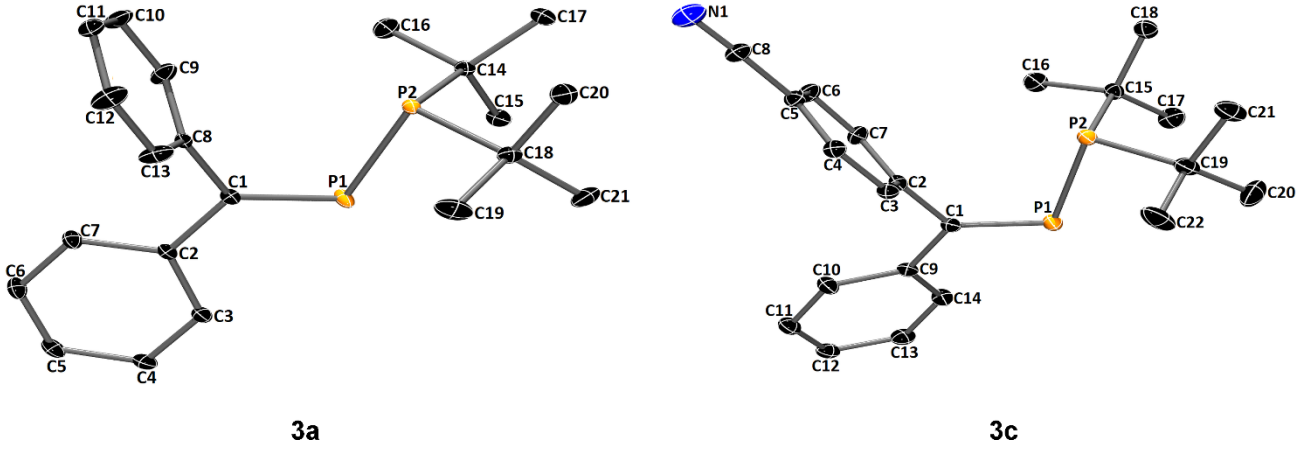


Figure 4. X-ray crystal structures of Ph_2C=P-P*t*Bu_2 (**3a**) and *Z*-(Ph)(4-CN-Ph) C=P–P*t*Bu2 (**3c**) (ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted, and carbon atoms are drawn as spheres for clarity). Selected distances and angles are shown in Table 2.

The P–P distances in **3a** (2.2121(7) Å), **3c** (2.2223(15) Å), **3d** (2.2224(7) Å, 2.176(8) Å), and **3e** (2.2115(12) Å) are similar to each other and are consistent with a single bond between two phosphorus atoms. The observed P–P distances are slightly longer than those in the starting lithium salts of diphosphane: $[Li(THF)_3P(SiMe_3)–P$*t*$Bu_2]$ (2.178(2) Å), $Li(12\text{-crown-}4)_2]^+[(SiMe_3)P–P$*t*$Bu_2]^-$ (2.1657(9) Å),[49] but are comparable to the distances observed in the diphosphanes: $Ph_2P–PPh_2$ (2.2217(1) Å),[68] Me_2P-PMe_2 (2.212(1) Å),[69] Cy_2P-PCy_2 (2.215(3) Å).[70] The P1=C1 distances in **3a**, **3c**, **3d** and **3e** (from 1.696(4) Å to 1.707(3) Å) are comparable to those observed in the literature and are in the typical P=C range for C-substituted phosphaalkenes (1.61-1.71 Å),[66, 71] at its upper limit. In **3c**, the P=C bond is the longest in the presented group; however, elongation of the P-C bond was also observed by Gates and coworkers in MesP=CPh(4-$OMeC_6H4$) 1.7082(13) Å.[56] The C1=P1-P2 angles are also close to each other and range from 103.57(14)° (*Z* isomer of **3c**) to 104.92(7)° (**3d**). In comparison to the C=P-C angles observed in the currently known structures of phosphaalkenes (from 108.5(2)° MesP=C(5-dibenzosuberenyl) to 104.1(1)° Mes*P=CH_2),[26, 66] the angles observed in our presented phosphanylphosphaalkenes are similar to or slightly below these values.

Table 2. Selected distances (Å) and angles (deg) of obtained phosphanylphosphaalkenes.

	C1=P1 [Å]	P1–P2 [Å]	C1=P1–P2 [°]
3a	1.6983(19)	2.2121(7)	103.84(7)
3c_*Z*	1.696(4)	2.2223(15)	103.57(14)
3d	1.697(2)	2.2224(7)	104.92(7)
	1.691(2)	2.2176(8)	103.94(7)
3e	1.707(3)	2.2115(12)	103.66(11)
4d_*E*	1.705(7)	2.195(2)	99.2(2) 98.7(2)
	1.677(6)	2.207(2)	
4e_*E*	1.680(4)	2.2079(16)	99.77(15)

After the reaction of **2** with aldehydes, two phosphanylphosphaalkenes were isolated in crystalline form: *E*-{$(Me)_2$N-Ph}(H)C=P-P*t*Bu_2 (**4d**) and *E*-PhPh(H)C=P-P*t*Bu_2 (**4e**). Both phosphanylphosphaalkenes crystallize in monoclinic space groups: C_2/c (**4d**) and $I_2/_a$ (**4e**). The molecular structures of both phosphanylphosphaalkenes are presented in Figure 5.

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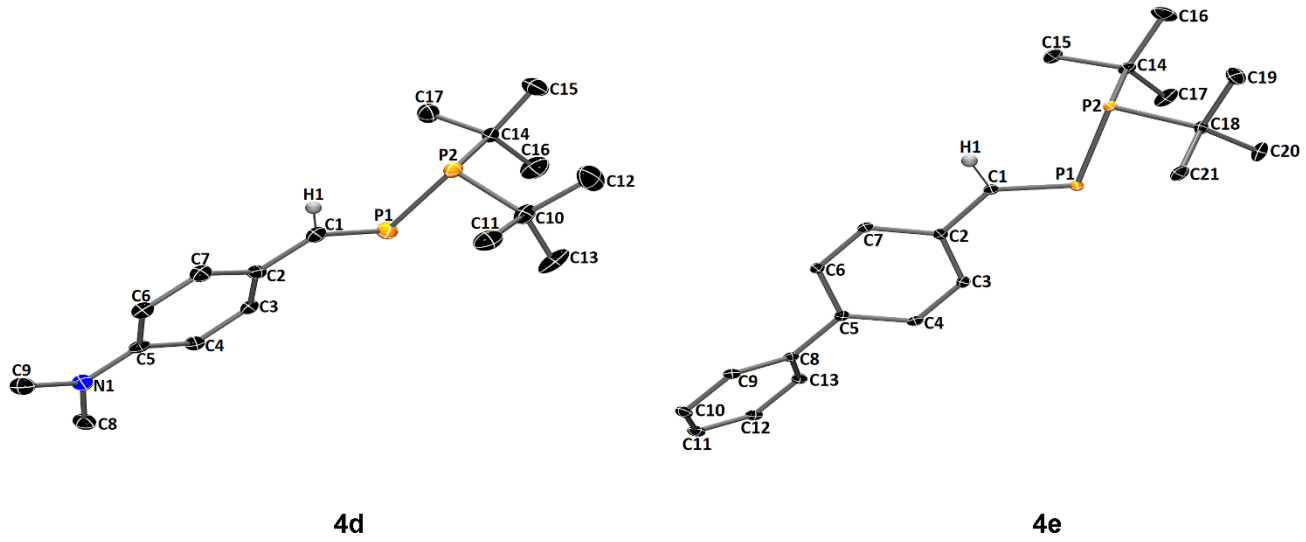

4d **4e**

Figure 5. X-ray crystal structures of *E*-{(Me)$_2$N-Ph}(H)C=P-P*t*Bu$_2$ (**4d**) and *E*-PhPh(H)C=P-P*t*Bu$_2$ (**4e**) (ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted, and carbon atoms are drawn as spheres for clarity). Selected distances and angles are shown in Table 2.

The P-P (1.705(7) Å, 1.677(6) Å, and 1.680(4) Å) and P=C (2.195(2) Å, 2.207(2) Å, and 2.2079(16) Å) distances observed in **4d** and **4e** are comparable to those in phosphanylphosphaalkenes **3a**, **3c**, **3d**, and **3e**, while the C=P-P angle decreased slightly (99.2(2)°, 98.7(2)° for **4d** and 99.77(15) for **4e**). Analogously, a reduction in this angle was observed in the phosphaalkenes, in which an aldehyde proton was present: Mes*C=P(H)Ph (100.9(3)°) and Mes*C=P(H)(*o*-C5H5N) (99.1(5)°).[33, 72]

Conclusions

The two methods we presented for the synthesis of phosphanylphosphaalkenes showed both advantages and disadvantages. The first method, metal-phospha-Wittig, allowed us to obtain a large range of compounds with a C=P-P moiety. However, its main limitation is the steric hindrance of the substituents in the ketones, which directly affect the difficult distillation process. To accurately explain the problem, we performed a theoretical investigation, which revealed that the phospha-Wittig-based approach to the synthesis of C=P-P bond systems is thermodynamically favored; however, kinetic rather than thermodynamic factors account for the effective reaction progress, facilitating the formation of phosphanylphosphaalkenes derived from carbonyls bound with sterically nondemanding substituents and/or bearing highly nucleophilic O atoms together with poorly electrophilic C atoms in the C=O group. Reactions involving carbonyls that do not satisfy these conditions have high energy barriers precluding the effective conversion of substrates into products. In the second method, the phospha-Peterson reaction was considered to be complementary to the first method. However, in reactions with ketones bearing alpha protons, the reactions proceed in the opposite direction (no phosphanylphosphaalkenes are formed). Nevertheless, optimization of this method facilitated the isolation of an oil of the following compounds: **3b**, **4a**, **4b**, and **4c**. Moreover, we isolated seven compounds in crystalline form (**3a**, **3c**, **3d**, **3e**, **3f**, **4d** and **4e**). The obtained phosphanylphosphaalkenes were stable in air and were not susceptible to hydrolysis. Importantly, these compounds open a wide perspective for further research (formation of new polymers with still reactive P-P bond, and activation the P-P bonds in the obtained polymers) not only due to their stability but also because of the presence of a diphosphoroorganic group and a reactive C=P bond.

Conflicts of interest

"There are no conflicts to declare".

Acknowledgements

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Notes and references

1. M. Regitz, Phosphaalkynes: new building blocks in synthetic chemistry, *Chem. Rev.*, 1990, **90**, 191-213.
2. F. Mathey, Expanding the analogy between phosphorus-carbon and carbon-carbon double bonds, *Acc. Chem. Res.*, 1992, **25**, 90-96.
3. P. Rosa, C. Gouverd, G. Bernardinelli, T. Berclaz and M. Geoffroy, Phosphaalkenes with Inverse Electron Density: Electrochemistry, Electron Paramagnetic Resonance Spectra, and Density Functional Theory Calculations of Aminophosphaalkene Derivatives, *J. Phys. Chem. A.*, 2003, **107**, 4883-4892.
4. L. Weber, Phosphaalkenes with Inverse Electron Density, *Eur. J. Inorg. Chem.*, 2000, **2000**, 2425-2441.
5. P. L. Floch, Phosphaalkene, phospholyl and phosphinine ligands: New tools in coordination chemistry and catalysis, *Coord. Chem. Rev.*, 2006, **250**, 627-681.
6. M. J. Hopkinson, H. W. Kroto, J. F. Nixon and N. P. C. Simmons, The detection of unstable molecules by microwave spectroscopy: phospha-alkenes CF_2=PH, CH_2=PCl, and CH_2=PH, *J. Chem. Soc., Chem. Commun.*, 1976, 513-515.
7. G. Becker, Bildung und Eigenschaften von Acylphosphinen. I. Monosubstitutionsreaktionen an substituierten Disilylphosphinen mit Pivaloylchlorid, *Z. Anorg. Allg. Chem.*, 1976, **423**, 242-254.
8. V. A. Wright and D. P. Gates, Poly(p-phenylenephosphaalkene): A π-Conjugated Macromolecule Containing P=C Bonds in the Main Chain, *Angew. Chem.*, 2002, **114**, 2495-2498.
9. A. Marinetti and F. Mathey, A Novel Entry to the PC-Double Bond: the "Phospha-Wittig" Reaction, *Angew. Chem, Int. Ed.*, 1988, **27**, 1382-1384.
10. M. Yoshifuji, K. Toyota, I. Matsuda, T. Niitsu, N. Inamoto, K. Hirotsu and T. Higuchi, Synthesis and structures of E- and Z-phosphaethylenes, *Tetrahedron*, 1988, **44**, 1363-1367.
11. K. Issleib, H. Schmidt and H. Meyer, Phospha-amidine, *J.Organomet. Chem.*, 1978, **160**, 47-57.
12. K. Dimroth and P. Hoffmann, Phosphacyanines, a New Class of Compounds Containing Trivalent Phosphorus, *Angew. Chem. Int. Ed.*, 1964, **3**, 384-384.
13. M. Yoshifuji, K. Toyota, N. Inamoto, K. Hirotsu and T. Higuchi, The first x-ray structure determination of a z-phosphaethylene: z-2-phenyl-1-(2,4,6-tri-t-butylphenyl)phosphaethylene, *Tetrahedron Lett.*, 1985, **26**, 6443-6446.
14. T. A. Van Der Knaap, T. C. Klebach, F. Visser, F. Bickelhaupt, P. Ros, E. J. Baerends, C. H. Stam and M. Konijn, Synthesis and structure of aryl-substituted phospha-alkenes, *Tetrahedron*, 1984, **40**, 765-776.
15. J. Mahnke, A. Zanin, W.-W. du Mont, F. Ruthe and P. G. Jones, The New P-Phosphanylphosphaalkene 1-Bis(trimethylsilyl)methylidene-2,2-diisopropyldiphosphane: First Reactions at its P=C and P-P Bonds, *Z. anorg. allg. Chem.*, 1998, **624**, 1447-1454.
16. T. L. Breen and D. W. Stephan, Phosphinidene Transfer Reactions of the Terminal Phosphinidene Complex $Cp_2Zr(:PC_6H_2$-2,4,6-*t*-$Bu_3)(PMe_3)$, *J. Am. Chem. Soc.*, 1995, **117**, 11914-11921.
17. R. O. Day, A. Willhalm, J. M. Holmes, R. R. Holmes and A. Schmidpeter, How is Phosphorus Bound in 2-Phospha- and 2-"Phosphoniaallyl" Cations?, *Angew. Chem. Int. Ed.*, 1985, **24**, 764-765.
18. A. Schmidpeter, W. Gebler, F. Zwaschka and W. Sheldrick, The =PCN Group as a Pseudochalcogen; Cyanophosphinidene Substituted Heterocycles, *Angew. Chem.*, 1980, **19**, 722-723.
19. R. R. Rodrigues, C. L. Dorsey, C. A. Arceneaux and T. W. Hudnall, Phosphaalkene vs. phosphinidene: the nature of the P–C bond in carbonyl-decorated carbene → PPh adducts, *Chem. Commun.*, 2014, **50**, 162-164.
20. D. Morales Salazar, E. Mijangos, S. Pullen, M. Gao and A. Orthaber, Functional small-molecules & polymers containing P=C and As=C bonds as hybrid π-conjugated materials, *Chem. Commun.*, 2017, **53**, 1120-1123.
21. J. I. Bates, J. Dugal-Tessier and D. P. Gates, Phospha-organic chemistry: from molecules to polymers, *Dalton Trans.*, 2010, **39**, 3151-3159.
22. D. P. Gates, in *New Aspects in Phosphorus Chemistry V: -/-*, ed. J.-P. Majoral, Springer Berlin Heidelberg, Berlin, Heidelberg, 2005, pp. 107-126.
23. C.-W. Tsang, M. Yam and D. P. Gates, The Addition Polymerization of a PC Bond: A Route to New Phosphine Polymers, *J. Am. Chem. Soc.*, 2003, **125**, 1480-1481.
24. C.-W. Tsang, C. A. Rohrick, T. S. Saini, B. O. Patrick and D. P. Gates, Destiny of Transient Phosphenium Ions Generated from the Addition of Electrophiles to Phosphaalkenes: Intramolecular C−H Activation, Donor−Acceptor Formation, and Linear Oligomerization, *Organometallics*, 2004, **23**, 5913-5923.
25. P. W. Siu, S. C. Serin, I. Krummenacher, T. W. Hey and D. P. Gates, Isomerization Polymerization of the Phosphaalkene $MesP{=}CPh_2$: An Alternative Microstructure for Poly(methylenephosphine)s, *Angew. Chem.*, 2013, **125**, 7105-7108.
26. C.-W. Tsang, B. Baharloo, D. Riendl, M. Yam and D. P. Gates, Radical Copolymerization of a Phosphaalkene with Styrene: New Phosphine-Containing Macromolecules and Their Use in Polymer-Supported Catalysis, *Angew. Chem.*, 2004, **116**, 5800-5803.
27. L. Chandrasena, K. Samedov, I. McKenzie, M. Mozafari, R. West, D. P. Gates and P. W. Percival, Free Radical Reactivity of a Phosphaalkene Explored Through Studies of Radical Isotopologues, *Angew. Chem., Int. Ed.*, 2019, **58**, 297-301.
28. V. A. Wright, B. O. Patrick, C. Schneider and D. P. Gates, Phosphorus Copies of PPV: π-Conjugated Polymers and Molecules Composed of Alternating Phenylene and Phosphaalkene Moieties, *J. Am. Chem. Soc.*, 2006, **128**, 8836-8844.
29. R. C. Smith and J. D. Protasiewicz, Conjugated Polymers Featuring Heavier Main Group Element Multiple Bonds: A Diphosphene-PPV, *J. Am. Chem. Soc.*, 2004, **126**, 2268-2269.
30. M. C. Simpson and J. D. Protasiewicz, Phosphorus as a carbon copy and as a photocopy: New conjugated materials featuring multiply bonded phosphorus, *Pure Appl. Chem.*, 2013, **85**, 801-815.
31. Rhett C. Smith and John D. Protasiewicz, Systematic Investigation of PPV Analogue Oligomers Incorporating Low-

Coordinate Phosphorus Centres, *Eur. J. Inorg. Chem.*, 2004, **2004**, 998-1006.

32. X.-L. Geng and S. Ott, Acetylene-Expanded Dendralene Segments with Exotopic Phosphaalkene Units, *Chem. Eur. J.*, 2011, **17**, 12153-12162.

33. R. Appel, J. Menzel, F. Knoch and P. Volz, Niederkoordinierte Phosphor-Verbindungen. 42. Trennung und röntgenographische Strukturbestimmung der E,Z-Isomeren des 2,4,6-Tri(tert.butyl)phenyl-phenylmethylenphosphans, *Z. Anorg. Allg. Chem.*, 1986, **534**, 100-108.

34. J. Grobe, D. L. Van, B. Lüth and M. Hegemann, Reaktive E=C(p-p)π-Systeme, XXVI. Einfache Synthese für Methylenphosphane (Phosphaalkene) des Typs HP=C(F)NR_2 und das Phosphaalkin P≡C-N(*i*Pr)$_2$, *Chem. Ber.*, 1990, **123**, 2317-2320.

35. J. Grobe, D. Le Van, U. Althoff, B. Krebs, M. Dartmann and R. Gleiter, Reactive E=C(p-p)π-Systems. Part 27. Trifluoromethyl Phosphaalkenes of the Type F_3CP=C(OR)NR_2: Synthesis, Spectroscopic Investigations, and Ligand Properties, *Heteroat. Chem.*, 1992, **2**, 385-.

36. J. Grobe, D. L. Van, J. Nientiedt, B. Krebs and M. Dartmann, Reaktive E=C (p-p) π-Systeme, XIV. Synthese und Struktur von Phosphaalkenen des Typs F_3CP=C(F)NR_2, *Chem. Ber.*, 1988, **121**, 655-664.

37. A. N. Chernega, A. V. Ruban, V. D. Romanenko, L. N. Markovski, A. A. Korkin, M. Y. Antipin and Y. T. Struchkov, Peculiarities of p_π-p_π conjugation in aminosubstituted phosphaalkenes, *Heteroat. Chem.*, 1991, **2**, 229-241.

38. R. Appel, F. Knoll and I. Ruppert, Phospha-alkenes and Phospha-alkynes, Genesis and Properties of the (p-p)π-Multiple Bond, *Angew. Chem., Int. Ed.*, 1981, **20**, 731-744.

39. R. Appel, C. Casser, M. Immenkeppel and F. Knoch, Easy Synthesis of Phosphaalkenes by a Phosphorus-Analogous Isocyanide Reaction and an Atypical Crystal Structure of a Tetracarbonyl(phosphaalkene)iron Complex, *Angew. Chem., Int. Ed.*, 1984, **23**, 895-896.

40. V. D. Romanenko, T. V. Sarina, M. I. Povolotskii and L. N. Markovskii, P-di(tert-butyl)phosphino-C,C-bis(dialkylamino)methylene phosphine, *Zh. Obshch. Khim.*, 1985, **55**, 1437-1438.

41. B. F. Wicker, J. Scott, J. G. Andino, X. Gao, H. Park, M. Pink and D. J. Mindiola, Phosphinidene Complexes of Scandium: Powerful PAr Group-Transfer Vehicles to Organic and Inorganic Substrates, *J. Am. Chem. Soc.*, 2010, **132**, 3691-3693.

42. F. Basuli, J. Tomaszewski, J. C. Huffman and D. J. Mindiola, Four-Coordinate Phosphinidene Complexes of Titanium Prepared by α-H-Migration: Phospha-Staudinger and Phosphaalkene-Insertion Reactions, *J. Am. Chem. Soc.*, 2003, **125**, 10170-10171.

43. G. Zhao, F. Basuli, U. J. Kilgore, H. Fan, H. Aneetha, J. C. Huffman, G. Wu and D. J. Mindiola, Neutral and Zwitterionic Low-Coordinate Titanium Complexes Bearing the Terminal Phosphinidene Functionality. Structural, Spectroscopic, Theoretical, and Catalytic Studies Addressing the Ti–P Multiple Bond, *J. Am. Chem. Soc.*, 2006, **128**, 13575-13585.

44. U. J. Kilgore, H. Fan, M. Pink, E. Urnezius, J. D. Protasiewicz and D. J. Mindiola, Phosphinidene group-transfer with a phospha-Wittig reagent: a new entry to transition metal phosphorus multiple bonds, *Chem. Commun.*, 2009, 4521-4523.

45. C. C. Cummins, R. R. Schrock and W. M. Davis, Phosphinidenetantalum(V) Complexes of the Type [(N_3N)Ta=PR] as Phospha-Wittig Reagents, *Angew. Chem, Int. Ed.*, 1993, **32**, 756-759.

46. J. D. Masuda, K. C. Jantunen, O. V. Ozerov, K. J. T. Noonan, D. P. Gates, B. L. Scott and J. L. Kiplinger, A Lanthanide Phosphinidene Complex: Synthesis, Structure, and Phospha-Wittig Reactivity, *J. Am. Chem. Soc.*, 2008, **130**, 2408-2409.

47. Ł. Ponikiewski, A. Ziółkowska and J. Pikies, Reactions of Lithiated Diphosphanes R_2P–P($SiMe_3$)Li (R = *t*Bu and *i*Pr) with [^{Me}NacnacTiCl_2·THF] and [^{Me}NacnacTiCl_3]. Formation and Structure of TitaniumIII and TitaniumIV β-Diketiminato Complexes Bearing the Side-on Phosphanylphosphido and Phosphanylphosphinidene Functionalities, *Inorg. Chem.*, 2017, **56**, 1094-1103.

48. W. Domanska-Babul, J. Chojnacki, E. Matern and J. Pikies, Reactions of R_2P-P($SiMe_3$)Li with [(R_3P)$_2$PtCl_2]. A general and efficient entry to phosphanylphosphinidene complexes of platinum. Syntheses and structures of [(η^2-P=P*i*Pr$_2$)Pt(p-Tol$_3$P)$_2$], [(η^2-P=P*t*Bu$_2$)Pt(p-Tol$_3$P)$_2$], [{η^2-P=P(N*i*Pr$_2$)$_2$}Pt(p-Tol$_3$P)$_2$] and [{(Et$_2$PhP)$_2$Pt}$_2$P$_2$], *Dalton Trans.*, 2009, 146-151.

49. E. Sattler, E. Matern, A. Rothenberger, A. Okrut, P. Bombicz, I. Fernández and I. Kovács, From Neutral to Ionic Species: Syntheses and X-ray Crystallographic and Multinuclear NMR Spectroscopic Studies of Li···P($SiMe_3$)–P*t*Bu$_2$ and Its Solvent Complexes, *Eur. J. Inorg. Chem.*, 2014, **2014**, 221-232.

50. A. Ziółkowska, N. Szynkiewicz, J. Pikies and Ł. Ponikiewski, Synthesis of compounds with C–P–P and C=P–P bond systems based on the phospha-Wittig reaction, *Dalton Transactions*, 2020, **49**, 13635-13646.

51. A. Ziółkowska, N. Szynkiewicz and Ł. Ponikiewski, Molecular Structures of the Phospha-Wittig Reaction Intermediate: Initial Step in the Synthesis of Compounds with a C═P–P Bond as Products in the Phospha-Wittig Reaction, *Organometallics*, 2019, **38**, 2873-2877.

52. A. Ziółkowska, N. Szynkiewicz, A. Wiśniewska, J. Pikies and Ł. Ponikiewski, Reactions of (Ph)*t*BuP-P($SiMe_3$)Li·3THF with [(PNP)TiCl_2] and [^{Me}NacNacTiCl_2·THF]: synthesis of first PNP titanium(iv) complex with the phosphanylphosphinidene ligand [(PNP)Ti(Cl){η^2-P-P(Ph)*t*Bu}], *Dalton Trans.*, 2018, **47**, 9733-9741.

53. G. B. Nikiforov, H. W. Roesky, P. G. Jones, R. B. Oswald and M. Noltemeyer, A ligand influence on the stability of heterobimetallic complexes containing the Ti(μ-O)Al skeleton. Transformation of heterometallic systems to the homometallic Ti(IV) and Al(III) complexes, *Dalton Trans.*, 2007, 4149-4159.

54. K. Esfandiarfard, A. I. Arkhypchuk, A. Orthaber and S. Ott, Synthesis of the first metal-free phosphanylphosphonate and its use in the "phospha–Wittig–Horner" reaction, *Dalton Trans.*, 2016, **45**, 2201-2207.

55. V. B. Gudimetla, A. L. Rheingold, J. L. Payton, H.-L. Peng, M. C. Simpson and J. D. Protasiewicz, Photochemical E–Z Isomerization of meta-Terphenyl-Protected Phosphaalkenes and Structural Characterizations, *Inorg. Chem.*, 2006, **45**, 4895-4901.

56. M. Yam, J. H. Chong, C.-W. Tsang, B. O. Patrick, A. E. Lam and D. P. Gates, Scope and Limitations of the Base-Catalyzed Phospha-Peterson PC Bond-Forming Reaction, *Inorg. Chem.*, 2006, **45**, 5225-5234.

57. J. F. Allan, R. Nassar, E. Specht, A. Beatty, N. Calin and K. W. Henderson, Characterization of a Kinetically Stable, Highly Ordered, Octameric Form of Lithium tert-Butoxide and Its Implications Regarding Aggregate Formation, *J. Am. Chem. Soc.*, 2004, **126**, 484-485.
58. T. J. Boyle, T. M. Alam, K. P. Peters and M. A. Rodriguez, Structural Diversity of Lithium Neopentoxide Compounds, *Inorg. Chem.*, 2001, **40**, 6281-6286.
59. B. Kern, H. Vitze, M. Bolte, M. Wagner and H.-W. Lerner, Kristallstruktur des Lithium-Trimethylsilanolats $[Li_7(OSiMe_3)_7(THF)]$, *Z. Anorg. Allg. Chem.*, 2008, **634**, 1830-1832.
60. N. D'Imperio, A. I. Arkhypchuk, J. Mai and S. Ott, Triphenylphosphaalkenes in Chemical Equilibria, *Eur. J. Inorg. Chem.*, 2019, **2019**, 1562-1566.
61. J. I. Bates and D. P. Gates, P=C Bonds as Building Blocks for Three- and Four-Membered Heterocyclic Cations: Synthesis, Structures and Mechanistic Studies, *Chem. Eur. J.*, 2012, **18**, 1674-1683.
62. J. R. Goerlich, A. Fischer, P. G. Jones and R. Schmutzler, Organophosphorverbindungen mit tertiären Alkylsubstituenten. III*: Synthese und Reaktionen Di-1-adamantylsubstituierter Phosphorverbindungen; Kristallstruktur von Di-1-Adamantylphosphinsäurechlorid / Organophosphorus Compounds with Tertiary Alkyl Substituents. Ill: Synthesis and Reactions of Di-1-adam antyl-Substituted Phosphorus Compounds; Crystal Structure of Di-1-adam antylphosphinic Chloride, *Z. Naturforsch. B*, 1994, **49**, 801-811.
63. A. N. Butkevich, M. V. Sednev, H. Shojaei, V. N. Belov and S. W. Hell, PONy Dyes: Direct Addition of P(III) Nucleophiles to Organic Fluorophores, *Org. Lett.*, 2018, **20**, 1261-1264.
64. A. Ziółkowska, N. Szynkiewicz and Ł. Ponikiewski, Experimental and theoretical investigation of the reactivity of $[(BDI^*)Ti(Cl)\{\eta^2\text{-}P(SiMe_3)\text{-}PiPr_2\}]$ towards selected ketones, *Dalton Trans.*, 2021, **50**, 1390-1401.
65. B. W. Rawe, C. M. Brown, M. R. MacKinnon, B. O. Patrick, G. J. Bodwell and D. P. Gates, A C-Pyrenyl Poly(methylenephosphine): Oxidation "Turns On" Blue Photoluminescence in Solution and the Solid State, *Organometallics*, 2017, **36**, 2520-2526.
66. B. W. Rawe, C. P. Chun and D. P. Gates, Anionic polymerisation of phosphaalkenes bearing polyaromatic chromophores: phosphine polymers showing "turn-on" emission selectively with peroxide, *Chem. Sci.*, 2014, **5**, 4928-4938.
67. K. Subaru, N. Akitake, T. Kozo and Y. Masaaki, The Electronic Effects of Bulky Aryl Substituents on Low Coordinated Phosphorus Atoms in Diphosphenes and Phosphaalkenes by Functionalization at the Para Position, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 1110-1120.
68. A. Dashti-Mommertz and B. Neumüller, Gallium and Indium Arsanido Metalates: Compounds Derived from the Zinc Blende and Wurtzite Structure, *Z. Anorg. Allg. Chem.*, 1999, **625**, 954-960.
69. O. Mündt, H. Riffel, G. Becker and A. Simon, Element–Element-Bindungen, IV. Molekül-und Kristallstruktur des Tetramethyldiphosphans und -diarsans /Element–Element Bonds, IV. Molecular and Crystal Structure of Tetramethyldiphosphane and -diarsane, *Z. Naturforsch. B*, 1988, **43**, 952.
70. R. Richter, J. Kaiser, J. Sieler, H. Hartung and C. Peter, Kristall- und Molekulstruktur von Tetracyclohexylbiphosphin, *Acta Crystallogr. B*, 1977, **33**, 1887-1892.
71. S. C. Serin, G. R. Dake and D. P. Gates, Addition-Isomerization Polymerization of Chiral Phosphaalkenes: Observation of Styrene–Phosphaalkene Linkages in a Random Copolymer, *Macromolecules*, 2016, **49**, 4067-4075.
72. A. Jouaiti, M. Geoffroy and G. Bernardinelli, Synthesis of new chelating agents: Association of a phosphaalkene moiety with a pyridine, *Tetrahedron Lett.*, 1992, **33**, 5071-5074.