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Potassium Dimesitylphosphinite Catalyzed Intermolecular Hydrophosphorylation of Alkynes

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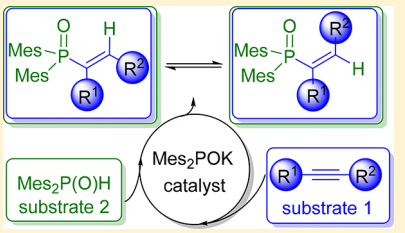
Supporting Information

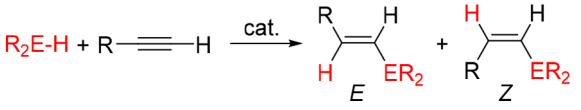
ABSTRACT: In this investigation we evaluated the scope of the intermolecular hydrophosphorylation (Pudovik reaction) of alkynes $R^1-C\equiv C-R^2$ (R^1 = H, alkyl, Ph; R^2 = alkyl, Ph, COOMe, $SiMe_3$, $Si(iPr)_3$) with bis(2,4,6-trimethylphenyl)phosphane oxide (dimesitylphosphane oxide, $Mes_2P(O)H$) in tetrahydrofuran at room temperature or 65 °C, catalyzed with 5 or 10 mol % of potassium dimesitylphosphinite (Mes_2P-O-K), yielding alkenyldimesitylphosphane oxides ($Mes_2P(O)-C(R^1)=C(H)R^2$). This procedure requires substituents with a −I effect at the C≡C triple bond, whereas alkyl-substituted alkynes are inactive under these reaction conditions. The hydrophosphorylation proceeds regioselectively, but *E*/*Z* isomer mixtures are obtained. *E*/*Z* isomerization occurs at elevated temperatures with an estimated energy barrier of 59 kJ mol^{-1} (R^1 = Me; R^2 = Ph). Trimethylsilyl substituents at the alkyne functionality (R^1 = H, *n*Bu; R^2 = $SiMe_3$) destabilize the product, leading to degradation and formation of $Mes_2P-O-SiMe_3$ and $R^1-C\equiv C-H$.



INTRODUCTION

Hydrofunctionalization reactions, i.e. addition of H−E bonds to multiple bonds, are atom-economical processes and depending on E these conversions are specified as hydroamination (E = N in amines), hydrophosphanylation (E = P in phosphanes), and hydrophosphorylation and hydrophosphonylation (E = P in phosphane oxides or sulfides as well as in phosphonates, Pudovik reaction), as depicted in Scheme 1.

Scheme 1. Hydrofunctionalization of Alkynes with Amines (E = N, Hydroamination), Phosphanes (E = P, Hydrophosphanylation, Hydrophosphination), and Phosphane Oxides and Sulfides (E = PO, PS, Hydrophosphorylation) Leading to *E*/*Z* Isomers



These reactions commonly require a catalyst because Lewis basic amines, phosphanes, and phosphane oxides have to interact with electron-rich multiple bonds such as alkenes, alkynes, and cumulenes. Furthermore, this procedure is entropically highly disfavored. Activation can be performed either via side-on coordination of the multiple-bond system at late transition metals or by deprotonation of the amines, phosphanes, and phosphane oxides with s-block or early transition metals (yielding amides, phosphanides, and phosphinites, respectively). Numerous recent reviews summarize the challenges and strategies related to the hydrofunctionalization of alkenes and alkynes.[1−4]

Recently, the potential of s-block metal-mediated catalysis in hydrofunctionalization reactions has been recognized.[5] The benefit of certain s-block metal catalysts is their environmentally benign character (especially of sodium, potassium, magnesium, and calcium). In addition, these electropositive metals form very Lewis acidic ions (depending on charge to radius ratios). Due to mainly ionic interactions in complexes of these highly electropositive alkali and alkaline-earth metals, regio- and stereocontrol of hydrofunctionalization represents a challenging task. A typical case is the calcium-mediated hydrophosphanylation of diphenylbutadiyne with diphenylphosphane, yielding regioisomeric mixtures.[6]

The intermolecular addition of P−H bonds to alkenes does not proceed very smoothly, and hence, the hydrophosphanylation of alkynes yields vinylphosphanes (Scheme 1, E = P).[6] Activation of the carbon atom in triple-bond systems and in cumulenes can be achieved by attached electronegative heteroatoms. Thus, heterocumulenes such as organic isocyanates can easily be hydrophosphorylated with calcium-[7,8] and potassium-based catalysts.[8,9] Furthermore, calcium-mediated hydrophosphorylation of acetonitrile and benzonitrile with diphenylphosphane oxide yields the doubly hydrophosphorylated products (see Scheme 2 and the Supporting Information), as also obtained from a very similar lanthanum-mediated catalysis.[10]

Whereas the hydrophosphorylation of nitriles and isocyanates proceeds smoothly with high yields,[7−9] addition of P−H bonds across alkenes and alkynes requires more drastic reaction conditions. With catalytic amounts of very strong bases such as lithium *tert*-butoxide a double addition of

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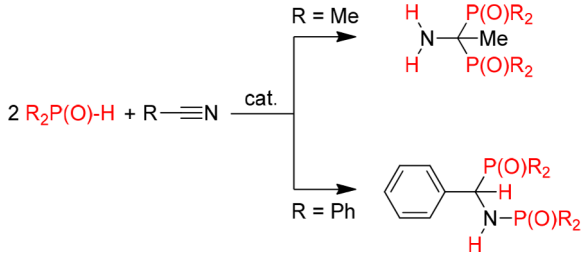
Organometallics XXXX, XXX, XXX−XXX

Scheme 2. Double Hydrophosphorylation of Acetonitrile (Top) and Benzonitrile (Bottom) with Diphenylphosphane Oxide Using Catalytic Amounts of $[(thf)_4Ca(PPh_2)_2]$



phosphine oxides to alkynes is feasible.[11] The role of the catalyst base has been evaluated earlier in the reaction of dialkyl phosphonate with ethyl propiolate, yielding various ratios of singly and doubly functionalized alkynes; pyridine is an unsuitable base because it is incorporated into the product.[12] On the basis of comparison studies, the reactivity of the P−H bond increases from dialkyl phosphonate to diphenylphosphane oxide to finally diphenylphosphane.[13] Due to the fact that strong bases act as catalysts, acid−base equilibria between the P−H species and the protonated catalyst may be assumed with the consequence that the pK_a values of the phosphonates, phosphane oxides, and phosphanes[14] in relation to the catalyst base are of significant importance.

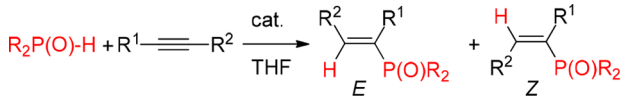
RESULTS AND DISCUSSION

Catalytic Hydrophosphorylation. Here we report the hydrophosphorylation of alkynes with bis(2,4,6-trimethylphenyl)phosphane oxide (dimesitylphosphane oxide). In an earlier study[9] the influence of steric hindrance on the catalytic activity of potassium phosphinites has been evaluated. We used the more bulky dimesitylphosphane oxide to ensure singly hydrophosphorylated products and to exclude competing doubly derivatized compounds. Furthermore, the proton NMR spectra are more meaningful due to a reduced overlap of resonances of the aryl groups with signals of the alkenyl moieties. We are studying catalysts based on nontoxic metals, and in this investigation, potassium bis(2,4,6-trimethylphenyl)phosphinite (K−O−PMes_2) was chosen because it was more reactive than the calcium congener in previous studies.[8]

In a typical procedure, we dissolved dimesitylphosphane oxide in tetrahydrofuran and added 0.05 or 0.1 equiv of potassium dimesitylphosphinite. To this yellow mixture was added a slight excess of alkyne dropwise because the removal of excess alkyne is easily achievable in vacuo, whereas an excess of dimesitylphosphane oxide requires a column chromatographic separation. To determine the conversion and progress of the hydrophosphorylation reaction yielding alkenyldimesitylphosphane oxides as shown in Scheme 3, ethanol was added to an aliquot of the reaction mixture to inactivate the catalyst. Then $CDCl_3$ was added and the reaction progress controlled by ^{31}P NMR spectroscopy.

The dependence of the conversion on the substituents at the alkyne is given in Table 1. In the absence of a catalyst no reaction occurs under these reaction conditions (entry 1). Substituents with a −I effect enabled the catalytic P−H addition of dimesitylphosphane oxide at the C≡C triple bond, whereas groups with a +I effect led to very small conversion

Scheme 3. Catalytic Hydrofunctionalization of Alkynes with Dimesitylphosphane Oxide Leading to *E*/*Z* Isomers



rates. Thus, quantitative conversion was observed for alkynes with phenyl (entries 2−4) and ester substituents (entry 5) but alkyl groups (entries 8−15) block this reaction regardless of the position of the alkyne unit, as demonstrated for 1-, 2-, and 3-hexyne (entries 8, 11, and 12, respectively). Variation of the solvent to toluene at 110 °C or use of the pure respective alkyne (without any additional solvent) did not improve conversion or yield. This finding is justified by the fact that electron-rich bases attack electron-rich multiple bonds and, hence, electron-poor alkynes are more easily accessible to this reaction. Even though heterocumulenes[7−9] and nitriles (see the Supporting Information) readily react with diarylphosphane oxide in the presence of phosphinite catalysts, the ester moiety (entry 5) was not functionalized under these reaction conditions.

The *E*/*Z* ratios of the alkenyldimesitylphosphane oxides strongly depend on the polarity of the solvent and the bulkiness of the group R^2. For the triisopropylsilyl derivative only the *E* isomer was observed. In a representative NMR experiment the hydrophosphorylation of phenylacetylene with dimesitylphosphane oxide showed the *E* and *Z* isomers of $Mes_2P(O)$-C(H)=C(H)Ph at around 23.8 and 21.2 ppm, respectively, with *E*/*Z* ratios of 9/1 in THF and of 2.7/7.3 in benzene (Figure 1).

Two further aspects require attention. The acidity of alkynes of the type R−C≡C−H may lead to side reactions due to competing acid−base (protonation−deprotonation) equilibria with the phosphinite catalyst, yielding R−C≡C−K and $Mes_2P(O)H$. Furthermore, alkynes with trimethylsilyl substituents show consumption of the substrates but no hydrophosphorylation product could be isolated.

Alkynes show pK_a values of approximately 21 (slightly depending on the method of determination and polarity of solvent),[15] and a very similar value of pK_a = 20.6 has been reported for diphenylphosphane oxide.[14] Therefore, equimolar amounts of phenylacetylene and potassium dimesitylphosphinite were mixed in $[D_8]$THF and investigated by ^{31}P NMR spectroscopy. Neither $Mes_2P(O)H$ nor starting Mes_2POK was observed; rather, there were small amounts of the addition product $Mes_2P(O)$−C(H)=C(H)Ph. This experiment verifies that "simple" Brønsted acid−base equilibria are less important.

The catalytic hydrophosphorylation of sterically protected triisopropylsilylacetylene with dimesitylphosphane oxide required long reaction periods of approximately 2 weeks in refluxing THF (Table 1, entry 7) to achieve a conversion of 87%. In contrast to this observation, less bulky (trimethylsilyl)-acetylene reacted much more quickly and a complete consumption of $Mes_2P(O)H$ was already detected after 2 days at room temperature (Table 1, entry 6). However, the hydrophosphorylation product did not form during this procedure; instead, a trimethylsilyl transfer occurred, leading to the formation of Mes_2P−O−$SiMe_3$ according to Scheme 4. Assuming a mechanism very similar to that proposed for the potassium phosphinite mediated hydrophosphorylation reaction, the close intramolecular vicinity of the trimethylsilyl group and the phosphoryl moiety enables the *O*-silylation,

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Organometallics XXXX, XXX, XXX−XXX

Table 1. Conversion of Substituted Alkynes R1−C≡C−R2 with Dimesitylphosphane Oxide in THF in the Presence of Catalytic Amounts of Potassium Dimesitylphosphinite[a]

entry	R^1	R^2	cat. (mol %)	T (°C)	t_{react} (h)	conversn (%)	E/Z ratio	yield (%)
1	H	Ph	0	100[b]	72	0		0
2	H	Ph	5	25	18	100	10/1	76
3	Me	Ph	5	65	72	100	2/3	54
4	Ph	Ph	5	65	96	100	2/1[c]	86
5	H	COOMe	5	25	0.5	100	2/3	81
6	H	$SiMe_3$	5	25	48	100		0
7	H	$Si(iPr)_3$	10	65	384	87	1/0	49
8	H	*n*Bu	5	65	600	4		0
9	H	*n*Hex	5	65	120	<2		0
10	H	Bz	5	65	136	<2		0
11	Me	*n*Pr	5	65	888	4		0
12	Et	Et	5	65	332	3		0
13	*n*Pr	*n*Pr	5	65	210	<2		0
14	*n*Bu	$SiMe_3$	5	65	235	46		0
15	*n*Bu	$Si(iPr)_3$	5	65	336	65		0

[a]The reaction time t_{react} is given in hours. Conversion was determined with an aliquot of the reaction solution after inactivation of the catalyst with ethanol. The yield refers to isolated pure compounds. Entry 1 is a control experiment without catalyst. [b]Reaction was performed in phenylacetylene. [c]Ratio was determined at 233 K due to fast E/Z isomerization at room temperature.

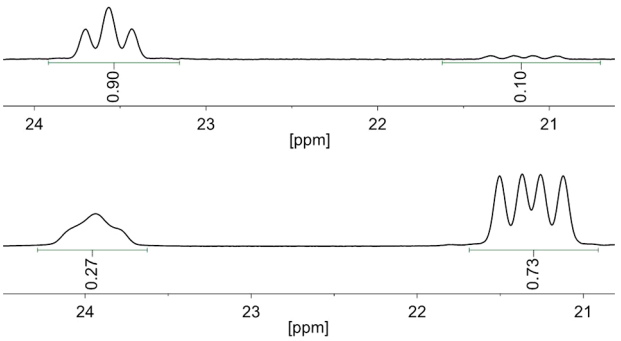
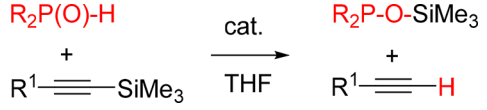


Figure 1. ^{31}P NMR spectra of the reaction solutions of 1 equiv of $Mes_2P(O)H$, 0.05 equiv of the catalyst Mes_2POK, and 1.1 equiv of phenylacetylene in [D_8]THF (top, 161.98 MHz, 297 K) and in [D_6]benzene (bottom, 161,98 MHz, 297 K).

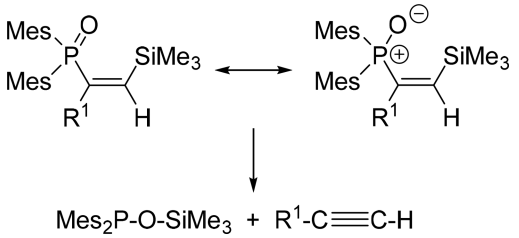
Scheme 4. Synthesis of (Trimethylsiloxy)dimesitylphosphane via *O*-Silylation of Dimesitylphosphane Oxide with (Trimethylsilyl)acetylene (R = Mes, R^1 = H, *n*Bu)



yielding $Mes_2P-O-SiMe_3$.[16] The significantly bulkier triisopropylsilyl group in (*E*)-$Mes_2P(O)-C(R^1)=C(H)-Si(iPr)_3$ avoids the close contact to the phosphane oxide functionality, and hence, the formation of a Si−O bond is prevented.

When the findings described above are taken into account, the catalytic cycle consists of the following steps. (i) The potassium dimesitylphosphinite adds to the alkyne $R^1-C\equiv C-R^2$, yielding $Mes_2P(O)-C(R^1)=C(K)R^2$. (ii) Protonation with dimesitylphosphane oxide re-forms the catalyst Mes_2POK and leads to the formation of alkenyldimesitylphosphane oxide $Mes_2P(O)$-$C(R^1)=C(H)R^2$. If R^2 is a trimethylsilyl group, a subsequent degradation pathway is proposed to explain the formation of (trimethylsiloxy)dimesitylphosphane (Scheme 5).

Scheme 5. Proposed Degradation Reaction of (Trimethylsilylethenyl)dimesitylphosphane Oxide (R^1 = H, *n*Bu)



Molecular Structures. For two representative examples the crystal structures were determined by X-ray diffraction experiments. The molecular structures of (*E*)-$Mes_2P(O)-C(H)=C(H)-Ph$ and (*Z*)-$Mes_2P(O)-C(H)=C(H)-COOMe$ are depicted in Figures 2 and 3, respectively.

The bonding parameters of both structures are very similar, and only small but significant differences can be observed. The P1−C1 bond length of the styryl derivative (*E*)-$Mes_2P(O)-C(H)=C(H)Ph$ is 2 pm smaller than that observed for the P1−C1 distance in the ester congener (*Z*)-$Mes_2P(O)-C(H)=C(H)-COOMe$. In both compounds the P1−C1 bond lengths are significantly smaller than the P1−C_{Mes} distances with an average value of 182.8 pm. Furthermore, also the C2−C3 bond of the alkenyl group of (*E*)-$Mes_2P(O)$-$C(H)=C(H)Ph$ is shorter, also suggesting a slight delocalization within the P−C=C−C unit of this compound leading to a nearly coplanar alignment of the phenyl and alkenyl π systems. The greater C2−C3 bond length in (*Z*)-$Mes_2P(O)-C(H)=C(H)-COOMe$ represents a typical value for a C−C single bond.

NMR Spectroscopy. In most of the catalytically mediated hydrophosphorylation products E/Z isomers were observed by NMR spectroscopy. Assignment of the NMR parameters to specific isomers is based on earlier studies that trans $^3J_{CP}$ coupling constants are greater than the cis values. Furthermore, the resonances of the *E* isomers are observed at lower field in comparison to those of the *Z* congeners; however, the shift

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Organometallics XXXX, XXX, XXX−XXX

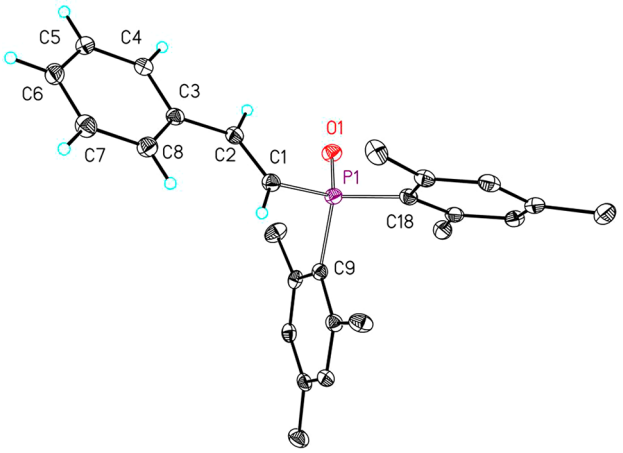

Figure 2. Molecular structure and numbering scheme of (*E*)-$Mes_2P(O)-C(H)=C(H)Ph$. The ellipsoids represent a probability of 30%. Only the hydrogen atoms of the styryl fragment are shown with arbitrary radii. Selected bond lengths (pm): P1–C1 179.68(15), P1–C9 183.05(15), P1–C18 182.26(15), P1–O1 148.61(11), C1–C2 133.5(2), C2–C3 147.2(2).

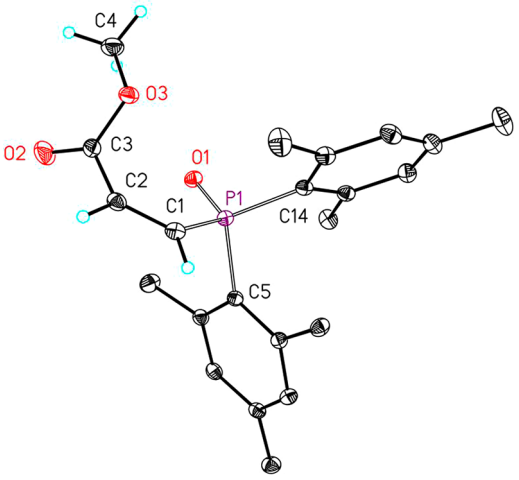

Figure 3. Molecular structure and numbering scheme of (*Z*)-$Mes_2P(O)-C(H)=C(H)-COOMe$. The ellipsoids represent a probability of 30%. Only the H atoms of the alkenyl moiety are shown with arbitrary radii. Selected bond lengths (pm): P1–C1 181.73(15), P1–C5 183.62(14), P1–C14 182.25(14), P1–O1 148.78(10), C1–C2 132.9(2), C2–C3 149.7(2), C3–O2 120.22(19), C3–O3 133.46(18), C4–O3 144.91(19).

differences $\Delta\delta(^{31}P)$ are quite small (5.5–8.4 ppm) for styryldiphenylphosphane oxides.[17] Another criterion for the assignment of the resonances to specific *E* and *Z* isomers is based on $^3J_{HH}$ coupling constants being larger for trans-positioned hydrogen atoms than for cis-arranged H atoms.[18]

Selected NMR parameters of the alkenyldimesitylphosphane oxides of the type $Mes_2P(O)-C(R^1)=C(H)R^2$ are given in Table 2. The shift differences $\Delta\delta(^{31}P)$ are small and have values of around 3 ppm. Much more significant are the vicinal $^3J_{HP}$ coupling constants which differ nearly by a factor of 2 for the *E* and *Z* isomers.

Another interesting feature concerns the *E*/*Z* isomerization which was observed at $Mes_2P(O)-C(Me)=C(H)Ph$. Commonly, cis–trans isomerization of alkenes represents a light-initiated process.[19] However, in this compound a thermal isomerization was studied with a [D_8]toluene solution by variable-temperature NMR experiments (Figure 4). Above

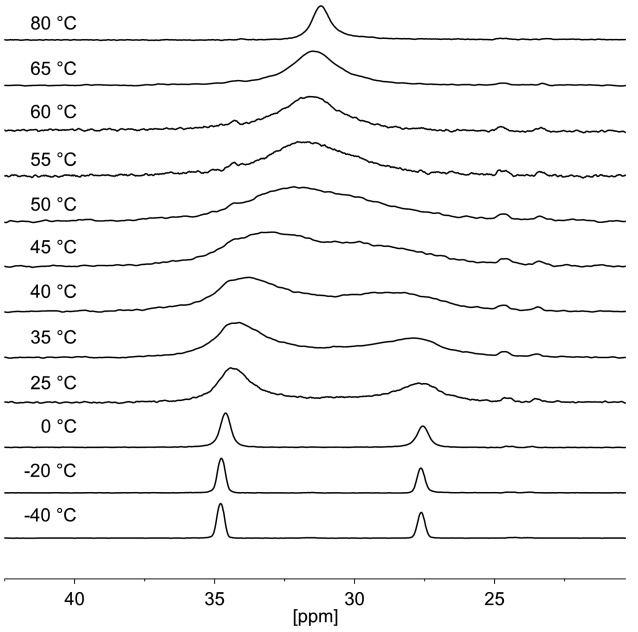

Figure 4. Variable-temperature ^{31}P NMR studies of $Mes_2P(O)-C(Me)=C(H)Ph$ showing the *E*/*Z* isomerization process at elevated temperature (161.98 MHz, [D_8]toluene).

room temperature a broad ^{31}P NMR resonance was observed at δ 31.2 ppm which became narrow at 80 °C and upon

Table 2. Selected ^{31}P and ^1H NMR Parameters ($CDCl_3$, 297 K) of Alkenyldimesitylphosphane Oxides of the Type $Mes_2P(O)-C(R^1)=C(H)R^2$ Prepared via Catalytic Hydrophosphorylation of Appropriate Alkynes with Dimesitylphosphane Oxide[a]

entry	R^1	R^2	isomer	$\delta(^{31}P)$	$\delta(^1H)_{\alpha\text{-}C}$	$^2J_{HP}$ (Hz)	$\delta(^1H)_{\beta\text{-}C}$	$^3J_{HP}$ (Hz)	$^3J_{HH}$ (Hz)
1	H	Ph	*Z*	23.2	na[b]	22.5	na[b]	40.2	na[b]
2	H	Ph	*E*	26.4	7.55	21.9	6.92	21.9	17.1
3	Me	Ph	*Z*	27.8			6.98	na[b]	
4	Me	Ph	*E*	35.0			6.98	na[b]	
5	Ph	Ph	*Z*	31.2			7.34	na[b]	
6	Ph	Ph	*E*	34.5			7.34	na[b]	
7	H	COOMe	*Z*	22.8	6.72	23.2	6.56	35.5	13.7
8	H	COOMe	*E*	23.8	7.68	24.4	6.90	16.6	16.6
9	H	$Si(iPr)_3$	*E*	24.1	7.22	30.8	7.09	34.5	20.0

[a]Chemical shifts are given in ppm. For the assignment of the parameters to specific isomers see the text. [b]Not assigned due to overlap with aryl resonances and due to low concentration.

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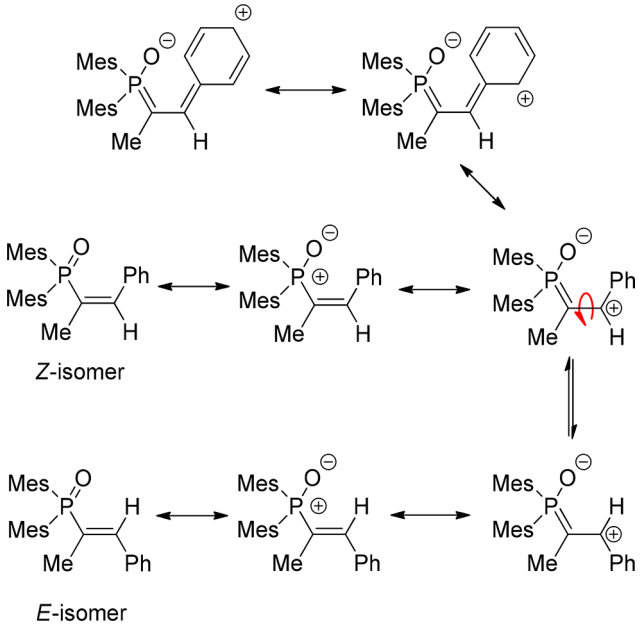
Organometallics XXXX, XXX, XXX–XXX

cooling two resonances at 34.8 and 27.6 ppm were found for the *E* and *Z* isomers. A rough estimation of the energy barrier of the *E*/*Z* isomerization process with the Gutowsky–Holm equation gave a value of 59 kJ mol^{-1}. A similar *E*/*Z* isomerization process was monitored for $Mes_2P(O)$–C(Ph)=C(H)Ph, whereas for $Mes_2P(O)$–C(H)=C(H)Ph only the *E* isomer was observed in $[D_8]$toluene. In contrast with these findings, the *E* and *Z* isomers of $Mes_2P(O)$–C(H)=C(H)–COOMe could be separated at room temperature by column chromatography.

The bulky dimesitylphosphoryl moiety is able to weaken the neighboring C=C double bond, as depicted in Scheme 6,

Scheme 6. Mesomeric Forms Explaining the Low Energy Barrier of the *E*/*Z* Isomerization Process at the Alkenyl Fragment[a]



[a]Rotation around the C–C bond is marked with a red arrow. The top mesomeric forms clarify the importance of the phenyl group in a β position.

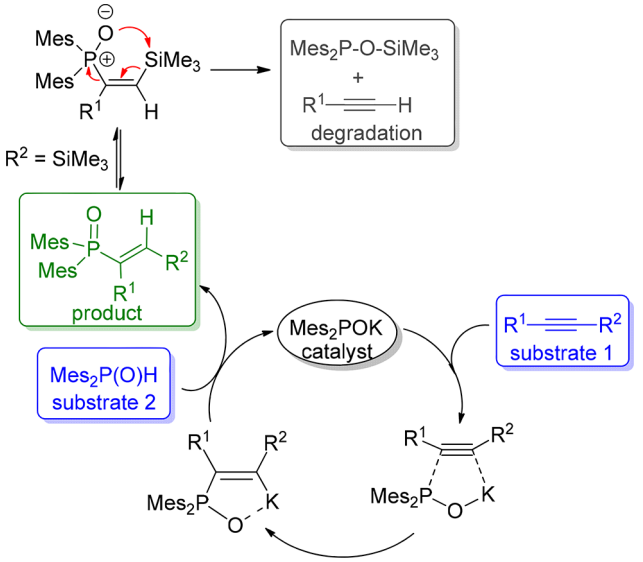
lowering the rotational barrier around the C=C bond of the alkenyl group. The phenyl group in a β position (R^2) additionally stabilizes the positive charge at the alkenyl group via delocalization into the aryl ring. Both factors synergistically weaken the C=C double-bond character and ease the rotation in the alkenyl moiety. Even though this charge delocalization obviously lowers the rotation barrier, the influence on the structural parameters is quite small but significant, leading to shorter P1–C1 bonds. Due to the fact that these dynamic NMR experiments were performed in the dark in the NMR spectrometer, we favor a thermal mechanism for the rotation around the C=C bond of the alkenyl unit rather than a radical photoisomerization process.

CONCLUSION

The hydrophosphorylation of alkynes (Pudovik reaction) with phosphane oxides requires a catalyst. In this study we elucidated the scope of the addition of dimesitylphosphane oxide across alkynes R^1–C≡C–R^2 (R^1 = H, alkyl, Ph; R^2 = alkyl, Ph, COOMe, $SiMe_3$, Si(*i*Pr)$_3$) in tetrahydrofuran at room temperature or at 65 °C. The initial reaction step requires the approach of an electron-rich phosphane oxide to an electron-rich multiple bond. To overcome electrostatic repulsion this addition reaction must be catalyzed. The potassium dimesitylphosphinite catalyst Mes_2POK is able to mediate the P–H addition at phenyl- and trialkylsilyl-substituted alkynes, whereas alkyl-substituted alkynes show no reactivity under these reaction conditions.

In Scheme 7 a catalytic cycle is proposed. The potassium phosphinite adds across the C≡C triple bond, yielding

Scheme 7. Proposed Catalytic Cycle for the Hydrophosphorylation of Alkynes R^1–C≡C–R^2 (R^1 = H, Alkyl, Ph; R^2 = Alkyl, Ph, $SiMe_3$, Si(*i*Pr)$_3$) with Dimesitylphosphane Oxide $Mes_2P(O)H$ in THF, Catalyzed by Potassium Dimesitylphosphinite[a]



[a]At the top the degradation of the trimethylsilyl-substituted compounds (R^2 = $SiMe_3$) is depicted.

$Mes_2P(O)$–C(R^1)=C(K)R^2. This complex is immediately protonated by dimesitylphosphane oxide, leading to the formation of $Mes_2P(O)$–C(R^1)=C(H)R^2 and the catalyst Mes_2POK is regained. If R^2 is the trimethylsilyl group, a subsequent degradation reaction yields Mes_2P–O–$SiMe_3$ and R^1–C≡C–H (R^1 = H, *n*Bu). This degradation reaction is prevented by the significantly bulkier triisopropylsilyl substituent because a close contact between the phosphane oxide moiety and the silicon atom is impossible.

The alkenyldimesitylphosphane oxides show thermal *E*/*Z* isomerization if R^2 is a phenyl group in conjugation with the alkenyl moiety (styryl derivatives). This finding can be explained by delocalization of positive charge within the P–C=C–aryl fragment, weakening the C=C double bond of the alkenyl group. The necessity of the aryl group is supported by a coplanar alignment of the phenyl group and the alkenyl moiety in the crystalline state.

EXPERIMENTAL SECTION

General Remarks. All manipulations were carried out under an inert nitrogen atmosphere using standard Schlenk techniques. The solvent was dried over KOH and subsequently distilled over sodium/benzophenone under a nitrogen atmosphere prior to use. Deuterated solvents were dried over sodium, degassed, and saturated with

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Organometallics XXXX, XXX, XXX–XXX

nitrogen. The yields given are not optimized. ^{1}H, $^{13}C\{^{1}H\}$, and ^{31}P NMR spectra were recorded on Bruker AC 400 and AC 600 spectrometers. Chemical shifts are reported in parts per million relative to $SiMe_4$ and phosphoric acid as external standards. The residual signals of the deuterated solvent $[D_8]$THF were used as internal standards for the interpretation of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra. Substrates were purchased from Sigma-Aldrich, Merck, or Alfa Aesar and used without further purification. The potassium dimesitylphosphinite catalyst was prepared according to a literature procedure.[9]

General Procedure. In a Schlenk flask 1.00 equiv of dimesitylphosphane oxide ($Mes_2P(O)H$) was dissolved in 20 mL of anhydrous THF and 0.05 or 0.10 equiv (R^2 = $Si(iPr)_3$) of potassium dimesitylphosphinite (Mes_2POK) was added. To this yellow solution was added an excess of alkyne at once. This reaction mixture was stirred at room temperature or at 65 °C (see Table 1) until a complete conversion was determined, as monitored by ^{31}P NMR spectroscopy of an aliquot of the reaction mixture after deactivation of the catalyst with ethanol. Thereafter, all volatile materials were removed in vacuo and the residue was extracted with $CHCl_3$ or CH_2Cl_2. Individual scheduled quantities, melting points, and spectroscopic parameters are summarized in the Supporting Information.

Structure Determinations. The intensity data were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semiempirical basis using multiple scans.[20−22] The structure was solved by direct methods (SHELXS[23]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[23]). The hydrogen atoms of (*E*)-$Mes_2P(O)$−C(H)=C(H)Ph as well as the alkenyl hydrogen atoms bonded to C1 and C2 of (*Z*)-$Mes_2P(O)$−C(H)=C(H)−COOMe were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[23] XP (SIEMENS Analytical X-ray Instruments, Inc.)[24] was used for structure representations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00368.

Scheduled quantities for the preparation of alkenyldimesitylphosphane oxides and NMR and IR spectra (PDF)

Accession Codes

CCDC 1844874−1844875 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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Organometallics XXXX, XXX, XXX−XXX