Inorganic Chemistry

Article

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Calcium-Mediated Catalytic Synthesis of 1-(Diorganylamino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-dienes

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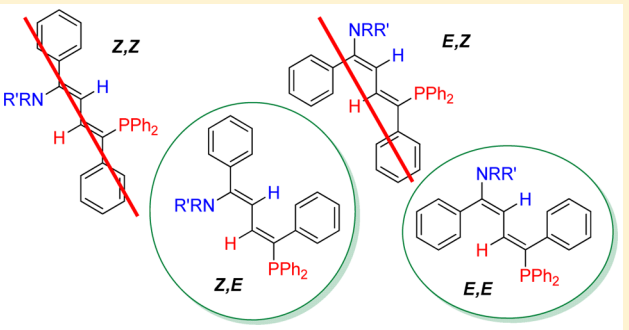
Supporting Information

ABSTRACT: The hydroamination of diphenylbutadiyne with 1 equiv of the secondary amines HNRR′ (R/R′ = Ph/Ph, Ph/Me, and pTol/Me) in the presence of catalytic amounts of the tetrakis(amino)calciate $K_2[Ca\{N(H)Dipp\}_4]$ (Dipp = 2,6-diisopropylphenyl) yields the corresponding 1-(diorganylamino)-1,4-diphenylbut-1-ene-3-ynes as a mixture of *E*/*Z* isomers. These tertiary alkenylamines react with diphenylphosphane to form RR′N−C(Ph)═CH−CH═C(Ph)−PPh_2 [R/R′ = Ph/Ph (**1**), Ph/Me (**2**), and pTol/Me (**3**)] in the presence of catalytic amounts of $[(THF)_4Ca(PPh_2)_2]$ or of the same calciate $K_2[Ca\{N(H)Dipp\}_4]$. Whereas the hydroamination is regio- (amino group in 1-position) but not stereoselective (formation of *E* and *Z* isomers), this second hydrofunctionalization step is regio- (phosphanyl group in 4-position) and stereoselective (only *E* isomers are formed), finally leading to mixtures of (*E*,*E*)- and (*Z*,*E*)-1-(diorganylamino)-1,4-diphenyl-4-(diphenylphosphanyl)-buta-1,3-dienes.



INTRODUCTION

Hydrofunctionalization (hydroelementation, hydropentelation) resembles an atom-economic addition of H−E bonds [E being the penteles N (hydroamination) and P (hydrophosphanylation)] to alkenes and alkynes; however, several challenges must be solved. Hydroamination and hydrophosphanylation represent only slightly exothermic reactions that are entropically disfavored. In addition, the approach of a Lewis base (primary or secondary amine and phosphane) to an electron-rich C═C and C≡C multiple bond is disadvantageous and requires an effective catalyst to overcome the electrostatic repulsion. Several strategies have been developed, and recently, alkaline earth metal-mediated hydropentelation catalysis has gained significant interest.[1−3] Calcium-based catalysts are especially attractive because these alkaline earth metals are globally abundant, inexpensive, easily available, and nontoxic.

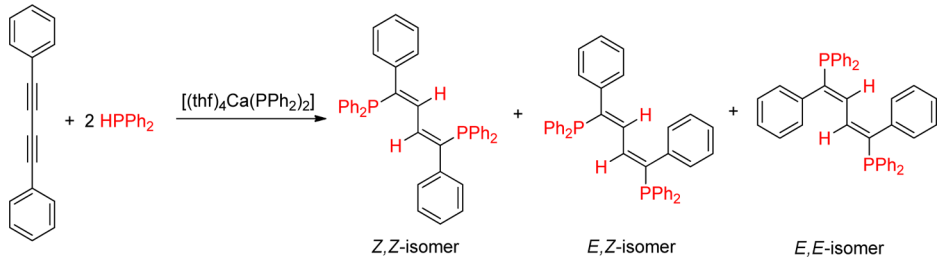
Intramolecular hydroamination of alkenes eliminates the entropic disadvantage and eases the addition of H−N bonds to C═C bonds. Calcium-based catalysts are able to catalyze this reaction, yielding azacycloalkanes.[4] Intermolecular hydroamination is achieved only with activated alkenes[5] and is much easier with C≡C bonds, requiring more reactive calcium-based catalysts correlated with the risk of also promoting undesired side reactions.[6] The reactivity of a calcium amide can be enhanced by the formation of a calciate. The catalyst should be coligand-free in order to avoid desolvation of the isolated crystalline compound due to uncontrolled loss of ligated Lewis bases such as ethers. This fact is important to allow an accurate ratio of catalyst to substrate. The heterobimetallic compound $K_2[Ca\{N(H)Dipp\}_4]$ (Dipp = 2,6-diisopropylphenyl) with a tetracoordinate calcium atom fulfills these requirements and hence represents an approved catalytically active calciate because this ether-free complex is soluble in ethereal solvents.[7]

The reaction pathway of primary amines H_2NR with butadiynes strongly depends on the reaction conditions and the *N*-bound substituent. Nevertheless, both N−H bonds are able to add to alkyne moieties, yielding either 2,5-substituted pyrroles at high reaction temperatures[8] or multicyclic imines at room temperature and prolonged reaction times.[7,8] Secondary amines can add only once; hence, cyclic products are avoided.[6,9] Thus, *N*-alkyl anilines add to one or both C≡C bonds of the butadiyne backbone, depending on the reaction time, the stoichiometry of the substrates, and the amount of calcium catalyst, yielding 1-aminobut-1-ene-3-yne or 1,4-diaminobuta-1,3-dienes, respectively. In contrast to this observation, secondary diphenylphosphane always adds twice to both C≡C bonds of the butadiyne unit in the presence of catalytic amounts of $[(THF)_4Ca(PPh_2)_2]$ (THF = tetrahydrofuran, Scheme 1).[10] Even a large excess of butadiyne leads to the formation of bis-phosphanylated compounds, and unreacted alkyne remains in the reaction mixture. The hydrophosphanylation of substituted butadiynes with diphenylphosphane yields primarily 1,4-bis(diphenylphosphanyl)-buta-1,3-dienes; however, other regioisomers such as 1,2-bis(diphenylphosphanyl)buta-1,3-dienes have also been observed. Neither the hydroamination nor the hydrophosphany-

Received: March 8, 2016

DOI: 10.1021/acs.inorgchem.6b00586
Inorg. Chem. XXXX, XXX, XXX−XXX

Scheme 1. Calcium-Mediated Hydrophosphanylation of Diphenylbutadiyne with Diphenylphosphane Yielding Isomeric Mixtures of 1,4-Bis(diphenylphosphanyl)buta-1,3-dienes



lation is stereoselective, but mixtures of *E* and *Z* isomers are formed.

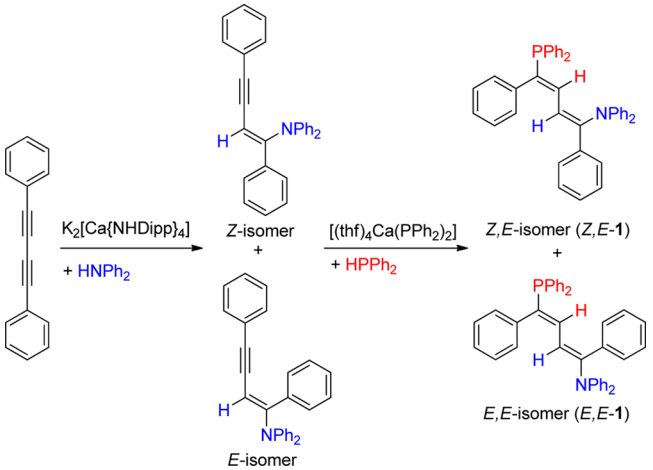
These findings suggest that the synthesis of substituted 1-amino-4-phosphanylbuta-1,3-dienes requires hydroamination as the initial step and hydrophosphanylation as a subsequent reaction. A further objective was the elucidation of the necessity to change the calcium-based catalyst from $K_2[Ca\{N(H)Dipp\}_4]$ for hydroamination to $[(THF)_4Ca(PPh_2)_2]$ for the following hydrophosphanylation. On the basis of the pK_a values of arylamines (approximately 31, depending on the substitution pattern), *N*-methyl-aniline (29.5), diphenylamine (25.0), and diphenylphosphane (22.9),[11] the calciate $K_2[Ca\{N(H)Dipp\}_4]$ is able to deprotonate secondary amines and diphenylphosphane, which is a precondition for the suitability of this calciate as a catalyst for hydropentelation reactions.

RESULTS AND DISCUSSION

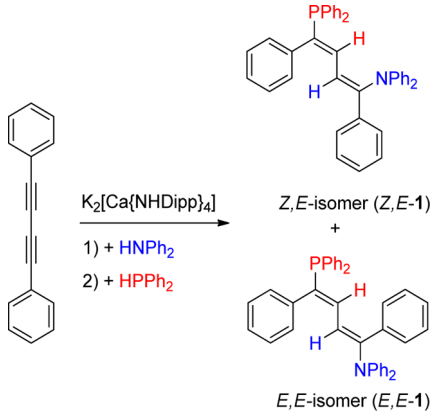
Synthesis and Catalysis. The singly hydroaminated *E* and *Z* isomers of 1-diphenylamino-1,4-diphenylbut-1-ene-3-yne[9] were hydrophosphanylated with diphenylphosphane in THF in the presence of 5 mol % $[(THF)_4Ca(PPh_2)_2]$, quantitatively yielding 1-diphenylamino-1,4-diphenyl-4-diphenylphosphanylbuta-1,3-diene (**1**) (Scheme 2). The conversion of the substrates was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The *E*/*Z* isomerism at the amino functionality was maintained, whereas only the *E*-isomeric hydrophosphanylation was observed. After complete reaction, the volume of the reaction mixture was reduced to half of the original volume, and the catalyst was destroyed with methanol. The hydropentelation product **1** was recrystallized from methylene chloride/pentane, giving yellow crystals of *E*/*E*-**1** and *Z*/*E*-**1**.

In another trial, the catalytic hydrophosphanylation of 1-diphenylamino-1,4-diphenylbut-1-ene-3-yne was repeated with catalytic amounts of $K_2[Ca\{N(H)Dipp\}_4]$. After complete conversion, the solvent was removed, and the residue was dissolved in methanol to inactivate the calcium catalyst. After removal of the methanol, the residue was dissolved in methylene chloride and filtered to remove the calcium-containing compounds. Thereafter, recrystallization from methylene chloride/pentane again provided yellow crystals of *E*/*E*-**1** and *Z*/*E*-**1** (Scheme 3). This result suggests that the two different hydroelementation reactions can be performed without a change in the catalyst system and without the need to isolate the hydroamination product prior to the hydrophosphanylation reaction.

Scheme 2. Two-Step Synthesis of 1-Diphenylamino-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (1) Using Different Calcium-Based Catalysts for the Hydropentelation Reactions



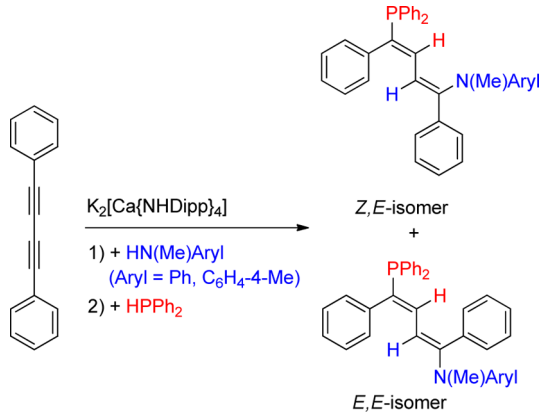
Scheme 3. Hydroamination and Hydrophosphanylation of Diphenylbutadiyne with the Same Catalyst $K_2[Ca\{N(H)Dipp\}_4]$



Because of the promising finding that $K_2[Ca\{N(H)Dipp\}_4]$ can promote hydroamination and hydrophosphanylation of diphenylbutadiyne, the hydroamination of diphenylbutadiyne was also performed with *N*-methyl-aniline and *N*-methyl-tolylamine as previously published with the catalyst $K_2[Ca\{N(H)Dipp\}_4]$.[9] Diphenylphosphane was added to this reaction mixture, yielding the appropriate hydrofunctionalization products 1-(*N*-methyl-anilino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (**2**) and 1-(*N*-methyl-tolylamino)-1,4-diphenyl-4-diphenylphosphanylbuta-1,3-diene (**3**) according to Scheme 4. Again, the initial hydroamination reaction gave an *E*/*Z*-isomeric mixture, whereas the hydrophosphanylation occurred regio- and stereoselectively to the *E*-isomeric hydrophosphanylation products.

DOI: 10.1021/acs.inorgchem.6b00586
Inorg. Chem. XXXX, XXX, XXX−XXX

Scheme 4. Calcium-Mediated Synthesis of 1-(*N*-Methylanilino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-dienes[a]



[a]Aryl = phenyl (**2**) or *p*-tolyl (**3**).

Isolation of the intermediate hydroamination product 1-amino-1,4-diphenylbut-1-ene-3-yne proved to be advantageous to prevent impurities such as bis-hydroaminated compounds. Unreacted butadiyne also had to be removed prior to the hydrophosphanylation procedures because otherwise the product would also contain bis-hydrophosphanylated derivatives. These side products hamper the isolation of analytically pure 1-amino-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene and hence lower the yields. Therefore, the preferred method involves an initial hydroamination reaction catalyzed by $K_2[Ca\{N(H)Dipp\}_4]$, followed by isolation and purification of 1-amino-1,4-diphenylbut-1-ene-3-yne. Thereafter, the hydrophosphanylation of this amine can be performed using catalytic amounts of either $[(THF)_4Ca(PPh_2)_2]$ or $K_2[Ca\{N(H)Dipp\}_4]$. In neither case were *E,Z*- and *Z,Z*-isomeric 1-amino-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-dienes observed. This finding is most probably the consequence of steric strain, but electronic effects may also play a minor role.

Molecular Structures. The molecular structures of (*E,E*)-1-diphenylamino-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (*E,E*-**1**) and (*Z,E*)-1-(*N*-methyl-anilino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (*Z,E*-**2**) are depicted in Figures 1 and 2, respectively, and the structures of *Z,E*-**1** and *Z,E*-**3** are represented in the Supporting Information. Selected structural parameters are compared in Table 1. Regardless of the isomerism, the structural parameters of these compounds are very similar. The butadiene fragment shows no delocalization, and typical C═C and C−C bond lengths of approximately 135 and 145 pm, respectively, are observed. For steric reasons, the planar amino group is twisted toward the planar butadiene plane; therefore, the electron pair at N cannot interact with the π-system of the butadiene moiety. In contrast to the amino group, the phosphorus atom is in a trigonal pyramidal environment with C−P−C bond angles of about 102°. Steric strain between the substituted end groups leads to a distortion of the C−C−C bond angles of the butadiene fragment. The C1−C2−C3 and C2−C3−C4 bond angles of *E,E*-**1** are significantly widened, whereas for all *Z,E* isomers, the enlargement of these bond angles is smaller. This finding verifies an intramolecular steric strain of the *Z,E* isomers smaller than that of the *E,E* derivatives. The lack of interaction between the phosphanyl end groups and the butadiene units leads to very similar P−C bonds of approximately 183 pm to the phenyl and butadiene moieties in all of these compounds, representing a characteristic P−C single-bond value.

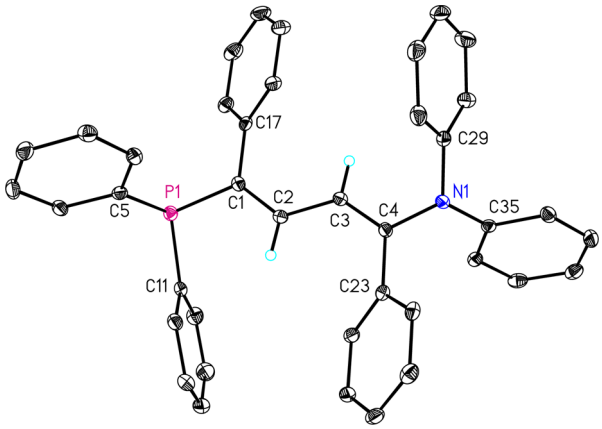


Figure 1. Molecular structure and numbering scheme of (*E,E*)-1-diphenylamino-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (*E,E*-**1**). The ellipsoids represent a probability of 30%; H atoms are shown with arbitrary radii.

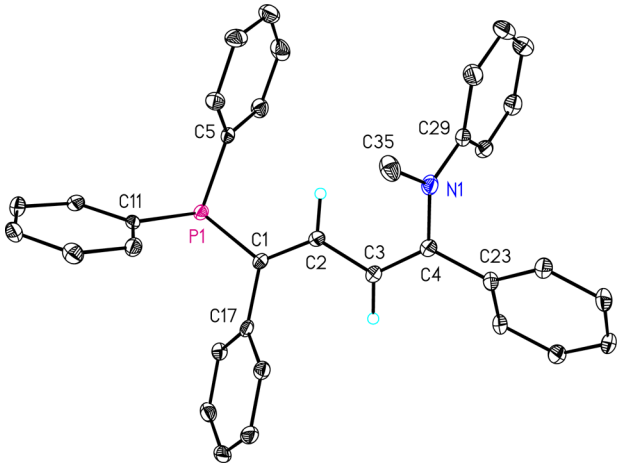


Figure 2. Molecular structure and numbering scheme of (*Z,E*)-1-(*N*-methyl-anilino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (*Z,E*-**2**). The ellipsoids represent a probability of 30%; H atoms are drawn with arbitrary radii.

NMR Spectroscopy. Selected NMR parameters of the 1-amino-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-dienes are compared in Table 2. The *E*/*Z* isomerism of the amino group has a small influence on the chemical shifts of the ^{31}P nuclei. Thus, the ^{31}P resonances of the *E,E* isomers are observed at nearly 5 ppm, whereas the *Z,E* isomers show chemical shifts of about 2.5 ppm. The carbon atoms of the butadiene backbone show low-field shifted signals between 135 and 156 ppm. Here, the amino-substituted C4 atoms lie at a field lower than that of the P-bound C1 atoms. The absolute values of the $^nJ_{C-P}$ coupling constants decrease with increasing *n* from approximately 22 Hz (*n* = 1) over 12 Hz (*n* = 2) to 2 Hz (*n* = 3). The vicinal $^3J_{H-H}$ and $^3J_{H-P}$ couplings of the hydrogen atoms at C2 and C3 also depend on the isomerism of the amino group with larger values for the *E,E* isomers.

In agreement with the structural data, the *Z,E*-isomeric forms are the major components, whereas the amount of *E,E* isomers is always significantly smaller. Therefore, we were able to isolate and crystallize the *Z,E* isomers of all reported derivatives,

DOI: 10.1021/acs.inorgchem.6b00586
Inorg. Chem. XXXX, XXX, XXX−XXX

Table 1. Selected Structural Parameters of 1-Diphenylamino-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (1), 1-(*N*-Methyl-anilino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (2), and 1-(*N*-Methyl-tolylamino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (3)

	E,E-**1**	*Z,E*-**1**	*Z,E*-**2**	*Z,E*-**3**
P1−C1	182.9(2)	183.6(2)	183.5(3)	182.7(4)
C1−C2	135.5(3)	134.6(2)	135.2(4)	134.0(6)
C2−C3	144.6(3)	145.0(2)	144.7(4)	144.8(6)
C3−C4	134.9(3)	135.3(2)	135.1(4)	135.6(6)
N1−C4	143.3(3)	142.3(2)	142.0(4)	141.4(5)
P1−C5	182.0(3)	183.6(2)	183.4(3)	182.9(5)
P1−C11	182.3(3)	182.9(2)	183.8(2)	182.9(4)
C1−C17	148.4(3)	148.4(2)	149.3(4)	149.6(6)
C4−C23	148.7(4)	147.6(2)	148.7(4)	148.0(6)
N1−C29	143.5(3)	141.5(2)	139.5(4)	141.2(6)
N1−C35	142.9(3)	142.6(2)	146.1(4)	145.0(6)
C1−P1−C5	102.1(1)	102.10(8)	102.2(1)	103.6(2)
C1−P1−C11	102.7(1)	102.11(8)	103.8(1)	102.7(2)
C5−P1−C11	103.9(1)	102.44(8)	102.5(1)	103.3(2)
P1−C1−C2	122.1(2)	121.7(1)	121.8(2)	123.0(3)
C1−C2−C3	125.2(2)	127.7(2)	126.9(3)	126.5(4)
C2−C3−C4	127.1(2)	122.3(2)	122.1(3)	124.8(4)
C3−C4−N1	118.8(2)	118.8(2)	120.7(2)	120.0(4)
C4−N1−C29	117.3(2)	120.1(1)	120.4(2)	120.8(3)
C4−N1−C35	117.7(2)	119.5(1)	119.5(3)	119.0(4)
C29−N1−C35	118.8(2)	120.1(1)	119.9(3)	118.8(4)

Table 2. Selected NMR Data of the *E,E* and *E,Z* Isomers of 1-Diphenylamino-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (1), 1-(*N*-Methyl-anilino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (2), and 1-(*N*-Methyl-tolylamino)-1,4-diphenyl-4-(diphenylphosphanyl)-buta-1,3-diene (3)

	E,E-**1**	*Z,E*-**1**	*E,E*-**2**	*Z,E*-**2**	*E,E*-**3**	*Z,E*-**3**
			^{1}H NMR			
δ(C2-*H*)	6.39	6.29	6.27	6.01	6.31	6.03
δ(C3-*H*)	6.62	6.45	6.49	6.51	6.49	6.42
^{3}J(H,H)	8.3	5.3	8.2	5.9	8.5	6.0
^{3}J(H,P)	12.1	10.7	11.6	10.9	11.5	10.9
δ(N-CH_3)			3.04	2.82	2.96	2.81
			^{13}C{^{1}H} NMR			
δ(C1)	140.6	140.4	141.8	141.1	140.3	142.4
^{1}J(C,P)	23.1	23.1	19.8	22.1	22.2	22.7
δ(C2)	136.4	135.0	136.2	136.2	136.1	135.5
^{2}J(C,P)	11.7	12.1	12.3	12.3	10.8	12.4
δ(C3)	146.7	145.7	147.5	147.5	146.6	147.0
^{3}J(C,P)	2.5	2.1	2.1	2.1	2.8	2.2
δ(C4)	147.5	147.1	151.6	149.5	152.0	156.0
δ(N-CH_3)			40.9	38.1	38	37.5
			^{31}P{^{1}H} NMR			
δ(*P*1)	4.45	2.54	4.70	2.28	4.96	2.35

whereas the parameters of the *E,E*-isomeric compounds had to be elucidated from isomeric mixtures.

Proposed Mechanism. On the basis of these findings, the catalytic cycle had to be formulated as a two-step reaction sequence, and the proposed mechanism is presented in Scheme 5. The initial catalytic cycle is depicted in the bottom part. After addition of the Ca−N bond, the intermediately formed alkenylcalcium complex **A** either deprotonates an amine (formation of the *E*-isomeric alkenylamine) or rearranges via intermediates **B** and **C** to the finally formed *Z*-alkenylamine. The necessity of obtaining the monohydroaminated products **D** and **E** limits the substitution pattern of the secondary amine substrates. For more reactive amines, the second calcium-mediated hydroamination of the other C≡C bond overlaps with the first hydroamination step, yielding mixtures of starting butadiyne and singly and doubly hydroaminated butadienes. In our hands, the above-utilized aniline derivatives represent the preferred substrates.[9] After complete conversion and preferably isolation of the alkenylamines, diphenylphosphane is added, immediately yielding the catalytically active calcium phosphanide species (L represents Lewis bases such as anionic amides and phosphanides or neutral amines, phosphanes, or ethers). The addition of the newly formed Ca−P bond to the remaining C≡C bond yields the intermediates **F** and **G** that immediately deprotonate the still-present diphenylphosphane. This hydrophosphanylation always leads to the formation of *E*-isomeric alkenylphosphanes, as shown in Scheme 5. In contrast to the calcium-mediated hydroamination, the catalytic hydrophosphanylation represents a very fast addition of a phosphane to an alkyne moiety. Under these reaction conditions, neither the amines nor the phosphanes react with the C=C bonds. The sequence of the catalytic steps (first hydroamination, then hydrophosphanylation) must be maintained because the phosphanes always add quantitatively to both C≡C bonds, invariably yielding doubly hydrophosphanylated derivatives.[10]

CONCLUSION

In summary, 1-amino- and 4-phosphanyl-substituted buta-1,3-dienes can be prepared and isolated in moderate to good yields from a calcium-mediated stepwise addition of secondary amines and phosphanes to butadiyne. Both of these hydrofunctionalization reactions can be promoted with the coligand-free calciate K_2[Ca{N(H)Dipp}$_4$] that is easily accessible and stable in the crystalline state as well as in ethereal solvents, allowing the preparation of stock solutions. After inactivation of the catalyst with methanol, pure 1-amino-4-phosphanylbuta-1,3-dienes are obtained by common workup procedures. Even though the same catalyst is used for both hydroelementation steps, the isolation of the intermediate 1-amino-1,4-diphenylbut-1-ene-3-yne is recommended to ease isolation of the pure end products.

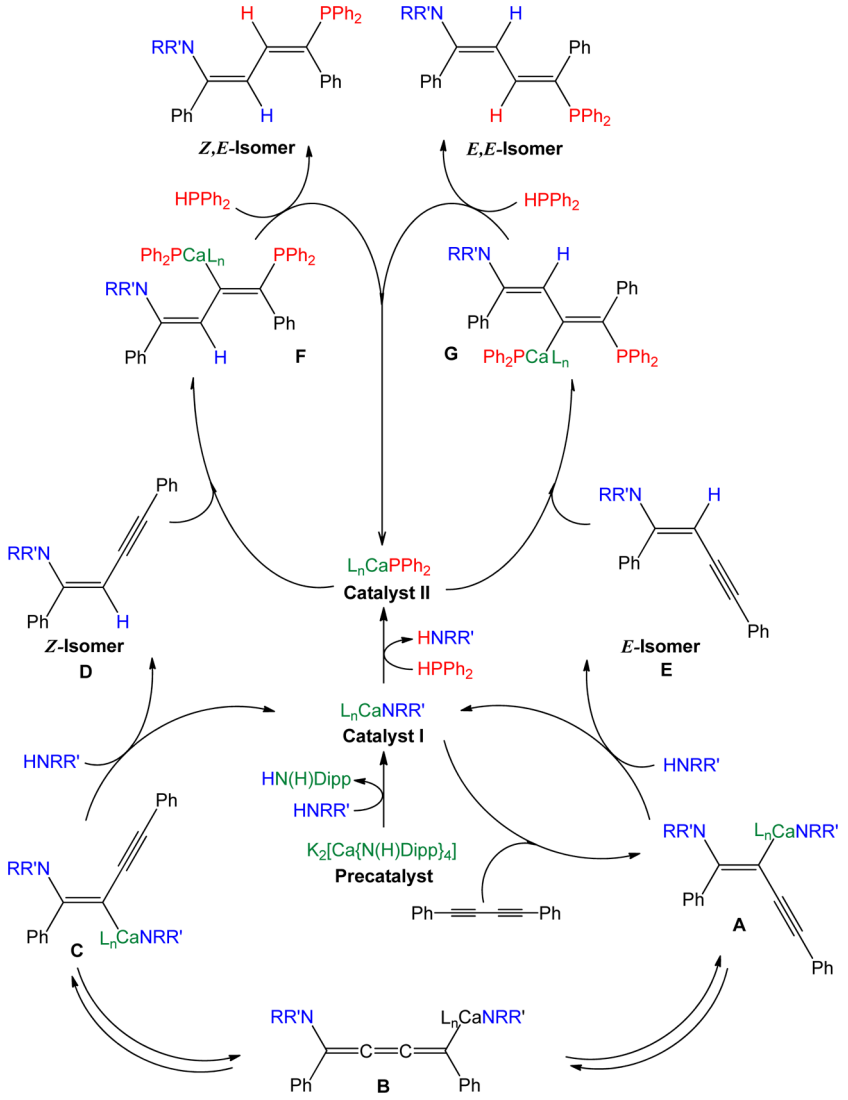
Dipotassium tetrakis(2,6-diisopropylanilino)calciate is an easy-to-handle and effective catalyst for the hydrofunctionalization of C≡C bonds in diphenylbutadiyne with both secondary amines and phosphanes, allowing the synthesis of 1-amino-1,4-diphenyl-4-phosphanylbuta-1,3-dienes. This calciate crystallizes as a coordination polymer; nevertheless, it is soluble in ethereal solvents, enabling the preparation of stock solutions. The crystalline compound and the stock solutions of this complex are stable and can be stored under anaerobic conditions. Both hydroelementation steps are regioselective, but only the catalytic addition of the H−P bond also stereoselectively yields the *E* isomer.

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under nitrogen using standard Schlenk techniques. The solvents were dried according to standard procedures prior to use. Deuterated solvents were dried over sodium, degassed, and saturated with nitrogen. The yields given are not optimized. ^{1}H, ^{13}C{^{1}H}, and

DOI: 10.1021/acs.inorgchem.6b00586
Inorg. Chem. XXXX, XXX, XXX−XXX

Scheme 5. Proposed Catalytic Cycle Shown as a Two-Step Process of Subsequent Hydroamination and Hydrophosphanylation Reactions[a]



[a]The bottom part shows the hydroamination and offers an explanation for the *Z*/*E* isomerism. In the second hydrophosphanylation catalysis, the amido ligand is substituted by the phosphanido group. The thus-formed Ca−P bond adds to the remaining alkyne moiety, followed by a metalation reaction. L represents a Lewis base such as amido or phosphanido anions or neutral Lewis bases such as ethers, amines, and phosphanes (see text).

$^{31}P\{^{1}H\}$ NMR spectra were recorded on Bruker Avance 200, Avance 400, and Avance 600 spectrometers. Chemical shifts are reported in parts per million. In some cases, $^{1}H,^{13}C\{^{1}H\}$-HSQC, $^{1}H,^{13}C\{^{1}H\}$-HMBC, and H,H-COSY NMR experiments were performed for the assignment of the resonances. For mass spectrometric investigations, the spectrometers ThermoFinnigan MAT95XL and Finnigan SSQ710 were used. IR spectra were recorded with a Bruker ALPHA FT-IR spectrometer. The starting amines and calcium-based catalysts $[(THF)_4Ca(PPh_2)_2]$ and $K_2[Ca\{N(H)Dipp\}_4]$ were prepared according to the literature protocols.

Synthesis of 1-Diphenylamino-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (1). In method A, 1-diphenylamino-1,4-diphenylbut-1-ene-3-yne (0.2 g, 0.54 mmol) was dissolved in 8 mL of THF. Diphenylphosphane (0.094 mL, 0.54 mmol) and 5 mol % $[(THF)_4Ca(PPh_2)_2]$ were added. The reaction mixture turned yellow immediately. After being stirred at rt for 2 h and under reflux for an additional 6 h, the volume was reduced to half of the original volume. A few milliliters of methanol were added, and the reaction mixture was stored at −15 °C. Yellow crystals of **3** (0.11 g, 0.2 mmol, 37%, mixture of isomers) precipitated and were collected. After a reduction of the volume of the mother liquor, another crop of crystals was obtained and isolated. In method B, to a solution of 1-diphenylamino-1,4-diphenylbut-1-ene-3-yne (0.140 g, 0.376 mmol) in THF (18 mL) were added diphenylphosphane (0.07g, 0.376 mmol) and 5 mol % calciate $K_2[Ca\{N(H)Dipp\}_4]$. The reaction mixture was stirred for 6 h at rt. Afterward, the solvent was removed in vacuo, and 10 mL of anhydrous methanol was added to inactivate the catalyst. Then, the methanol was removed, and 12 mL of dichloromethane was added. This solution was filtered over diatomaceous earth. Crystallization via the diffusion method (dichloromethane/pentane) at 5 °C yielded yellow crystals suitable for X-ray diffraction studies (0.14 g, 0.251 mmol, 67%, mixture of isomers). Mp: 138−142 °C. ^{1}H NMR (600 MHz, THF): δ 7.36 (d, J_{H-H} = 7.2 Hz, 2H), 7.31 (J_{H-H} = 7.7 Hz, 2H), 7.21−7.07 (m, 16H), 7.06−7.01 (m, 4H), 6.88 (m, 6H), 6.66 (d, $^{3}J_{H-H}$ = 7.5 Hz, 1H, *E*,*E*), 6.45 (d, $^{3}J_{H-H}$ = 10.7 Hz, 1H, *Z*,*E*), 6.39 (dd, $^{3}J_{H-P}$ = 12.1, 8.3 Hz, 1H, C2-*H E*,*E*), 6.29 (dd, $^{3}J_{H-P}$ = 10.7, 5.3 Hz, 1H, C2-*H Z*,*E*). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2): δ 147.5 (*C*4 *E*,*E*), 147.3 (*C*4 *Z*,*E*), 146.7 (d, $^{3}J_{C-P}$ = 2.5 Hz, *C*3 *E*,*E*), 145.9 (d, $^{3}J_{C-P}$ = 2.4 Hz, *C*3 *Z*,*E*), 144 (d, J_{C-P} = 16.5 Hz, *C*11,5), 143.4 (d, $^{2}J_{C-P}$ = 6.4 Hz), 140.6 (d, J_{C-P} = 23.1 Hz, *C*1 *E*,*E*), 139.8 (d, J_{C-P} = 23.1 Hz, *C*1 *Z*,*E*), 139.5, 139 (d, $^{2}J_{C-P}$ = 3.5 Hz), 136.4 (d, $^{2}J_{C-P}$ = 11.7 Hz, *C*2 *E*,*E*), 135 (d, $^{2}J_{C-P}$ = 11.6 Hz, *C*2 *Z*,*E*), 134.8, 134.6,

DOI: 10.1021/acs.inorgchem.6b00586
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134.18 (d, $^2J_{C-P}$ = 7.5 Hz), 133.5, 133.3, 129.8, 129.7, 129.4, 129.3, 129.2 (d, ^3J = 2.8 Hz), 129.1, 128.6 (d, $^2J_{C-P}$ = 7.3 Hz), 128.4, 127.8, 127.7, 127.7, 127.6, 126.8, 125.5, 125.1, 122.6 (d, $^3J_{C-P}$ = 2.0 Hz), 122.3, 122.2, 122.1, 122, 121.9, 121.78. ^{13}C NMR (151 MHz, [D$_8$]THF, *Z,E* isomer): δ 147.1 (*C*4), 145.7 (d, $^3J_{C-P}$ = 2.1 Hz, *C*3), 143.9 (d, J_{C-P} = 17.6 Hz, C11,5), 140.4 (d, J_{C-P} = 23.1 Hz, C1), 138.5, 135 (d, $^2J_{C-P}$ = 12.1 Hz, *C*2), 134.3, 134.2, 133.8 (d, $^2J_{C-P}$ = 7.9 Hz), 129.3 (d, $^2J_{C-P}$ = 9.3 Hz), 128.8, 128.5, 128.1, 128.1, 128, 127.8, 127.1, 127, 122 (d, $^2J_{C-P}$ = 1.7 Hz), 121.8, 121.5. ^{31}P{^{1}H} NMR (243 MHz, [D$_8$]THF): δ 2.54 (s, *Z,E* isomer), 4.49 (s, *E,E* isomer). Elemental analysis ($C_{40}H_{32}NP$, 557.21): Calcd C, 86.15; H, 5.78; N, 2.51; P, 5.55. Found: C, 83.79; H, 5.74; N, 2.51. MS (EI, *m*/*z*): 557 (60) [M], 389 (100) [M − $C_{12}H_{11}N$], 370 (10), 180 (100), 77 (25) [Ph]. IR: 3049 w, 3959 w, 2920 w, 1656 m, 1630 m, 1484 s, 1432 m, 1288 m, 1258 m, 1223 s, 1174 m, 1074 s, 1024 s, 859 m, 797 s, 761 s, 740 s, 690 vs, 602 m, 548 m, 496 s, 479 m.

Synthesis of 1-(*N*-Methyl-anilino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (2). To a solution of 1-(*N*-methyl-anilino)-1,4-diphenylbut-1-ene-3-yne (0.100 g, 0.323 mmol) in THF (17 mL) were added diphenylphosphane (0.06 g, 0.323 mmol) and 5 mol % calciate K_2[Ca{N(H)Dipp}$_4$]. The reaction mixture was stirred for 4 h at rt. After the consumption of all starting materials, all volatile materials were removed in vacuo, and 10 mL of anhydrous methanol was added to destroy the remaining catalyst. Afterward, the methanol was removed, and 12 mL of dichloromethane was added. Then, the solution was filtered over diatomaceous earth. Crystallization via the diffusion method (dichloromethane/pentane) at 5 °C gave single crystals in a yellow mother liquor (0.11 g, 0.222 mmol, 69%). Mp: 146−149 °C. ^{1}H NMR (600 MHz, [D$_8$]THF): δ 7.40 (m, 2H, Ar-*H*), 7.34 (d, *J* = 8.2 Hz, 1H, Ar-*H*), 7.31−7.13 (m, 24H, Ar-*H*), 6.70 (t, $^3J_{H-H}$ = 7.3 Hz, 1H, Ar-*H*), 6.62 (m, 2H, Ar-*H*), 6.51 (d, $^3J_{H-H}$ = 10.9 Hz, 1H,C3-*H*, *Z,E*), 6.27 (dd, $^3J_{H-P}$ = 11.6, 8.2 Hz, C2-*H*, *E,E*), 6.05−5.97 (dd, $^3J_{H-P}$ = 10.9, 5.9 Hz, 1H, C2-*H*, *Z,E*), 3.04 (s, 1H, C35-*H*, *Z,E*), 2.82 (s, 3H, C35-*H*, *Z,E*). ^{13}C{^{1}H} NMR (151 MHz, [D$_8$]THF): δ 151.6 (C4 *E,E*), 149.5 (*C*4 *Z,E*), 147.5 (d, $^3J_{C-P}$ = 2.1 Hz, *C*3 *Z,E*, *E,E*), 143.9 (d, $^3J_{C-P}$ = 7.6 Hz), 141.8 (d, $^1J_{C-P}$ = 19.8 Hz, *C*1 *E,E*), 141.1 (d, $^1J_{C-P}$ = 22.1 Hz, *C*1 *Z,E*), 139, 136.2 (d, $^2J_{C-P}$ = 12.3 Hz, *C*3 *Z,E*, *E,E*), 135.08 (d, $^2J_{C-P}$ = 20.6 Hz, C5,11), 134, 134.7, 134.6, 130.7, 130.3 (d, $^2J_{C-P}$ = 7.8 Hz, C17), 130.1 (d, $^2J_{C-P}$ = 8.7 Hz), 129.5, 129.4, 129.2, 129.1, 129.1, 129 (d, $^2J_{C-P}$ = 4.0 Hz), 129, 128.8, 128.8, 128.7, 128.5, 128.5, 128.3, 127.9, 127.3, 127, 123.1, 122.3, 121.5, 117.9, 114.2, 111.4, 40.9 (C35 *E,E* isomer), 38.1 (C35 *Z,E* isomer). ^{31}P{^{1}H} NMR (243 MHz, [D$_8$]THF): δ 4.70 (s, *E,E* isomer), 2.28 (s, *Z,E* isomer). Elemental analysis ($C_{35}H_{30}NP$, 495.57): Calcd C, 84.82; H, 6.10; N, 2.83; P, 6.25. Found: C, 84.54; H, 6.10; N, 2.86. MS (EI, *m*/*z*): 434 (90) [M], 389 (100) [M − C_7H_9N], 370 (50), 309 (30) [M − L], 183 (90), 118 (70) [$PhNC_2H_3$], 77 (25) [Ph]. IR: 3052 w, 2961 w, 2815 w, 2800 w, 1950 w, 1595 m, 1541 m, 1484 s, 1432 m, 1350 m, 1321 m, 1260 m, 1199 m, 1106 s, 1009 m, 885 m, 775 s, 746 vs, 688 vs, 598 m, 505 m, 498 m, 478 s.

Synthesis of 1-(*N*-Methyl-tolylamino)-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene (3). To a solution of (*N*-methyl)-(*N*-4-tolyl)-1,4-diphenylbut-1-ene-3-yne-1-ylamine (0.270 g, 0.834 mmol) in THF (17 mL) were added diphenylphosphane (0.156 g, 0.834 mmol) and 5 mol % calciate catalyst K_2[Ca{N(H)Dipp}$_4$], and the reaction mixture was stirred for 8 h at rt. After the reaction solvent was removed, 10 mL of dry methanol was added to deactivate the catalyst. Afterward, the methanol was removed; 12 mL of dichloromethane was added, and the solution was filtered over Celite. Recrystallization via the diffusion method (dichloromethane/pentane) at 5 °C yielded crystals in a yellow solution (0.3 g, 0.588 mmol, 71%). Mp: 147−152 °C. ^{1}H NMR (400 MHz, [D$_8$]THF): δ 7.43−7.34 (m, 2H), 7.30−7.10 (m, 18H), 6.99 (d, J_{H-H} = 8.2 Hz, 2H), 6.60−6.50 (m, 2H), 6.49 (d, $^3J_{H-H}$ = 7.6 Hz, 1H, C3-*H E,E*), 6.42 (d, $^3J_{H-H}$ = 10.9 Hz, 1H, C3-*H Z,E*), 6.31 (dd, $^3J_{H-P}$ = 11.5, 8.5 Hz, 1H, C2-*H E,E*), 6.03 (dd, $^3J_{H-P}$ = 10.9, 6.0 Hz, 1H, C2-*H Z,E*), 2.96 (s, 3H, C35-*H E,E*), 2.81 (s, 3H, C35-*H Z,E*), 2.27 (s, 3H, C36-*H E,E*), 2.25 (s, 3H, C36-*H Z,E*). ^{13}C{^{1}H} NMR (101 MHz, [D$_8$]THF, *Z,E* isomer): δ 156.2 (*C*4), 147 (d, $^3J_{C-P}$ = 2.2 Hz, *C*3), 142.4 (d, J_{C-P} = 22.3 Hz, *C*1), 138.4, 135.5 (d, $^2J_{C-P}$ = 12.4 Hz, *C*2), 134.5, 134, 129.3, 129.2, 128.5, 128.3, 128.2, 128.1, 127, 127.8, 126.9, 126.5, 125.8, 120, 113.7, 37.5 (*C*35), 19.6 (*C*36). ^{13}C{^{1}H} NMR (101 MHz, [D$_8$]THF, isomeric mixture): δ 156 (*C*4 *Z,E*), 152.8 (*C*4 *E,E*), 147.8 (d, $^3J_{C-P}$ = 2.2 Hz, *C*3 *Z,E*), 146.6 (d, $^3J_{C-P}$ = 2.8 Hz, *C*3 *E,E*), 142.4 (d, J_{C-P} = 22.7 Hz, *C*1 *Z,E*), 140.3 (d, J_{C-P} = 22.0 Hz, *C*1 *E,E*), 139.1 (d, $^2J_{C-P}$ = 12.4 Hz, *C*2 *Z,E*), 138.2, 136.9 (d, $^3J_{C-P}$ = 2.3 Hz), 136.1 ($^2J_{C-P}$ = 10.8 Hz, *C*2 *E,E*), 135.5 (d, $^2J_{C-P}$ = 12.4 Hz, *C*2 *Z,E*) 135.4, 135.2, 135.1, 134.3, 134.2, 134.1, 133.3, 132.3, 131.9 (d, $^2J_{C-P}$ = 9.1 Hz), 131.4, 131.5 (d, $^2J_{C-P}$ = 5.1 Hz), 130.8 (d, $^3J_{C-P}$ = 2.7 Hz), 130.5, 130.3 (d, $^2J_{C-P}$ = 4.8 Hz), 130.1, 129.4, 129.2, 129.1, 129, 128.8, 128.5, 128.5, 128.4, 128.3, 128.2, 128.1 (d, $^3J_{C-P}$ = 2.7 Hz), 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.2, 127, 126.5, 125.8, 125, 120 (d, $^3J_{C-P}$ = 2.3 Hz), 119.7, 117.7, 117.6, 114.5, 113.6, 38 (*C*35 *Z,E*), 37.4 (*C*35 *E,E*), 19.7 (*C*36 *Z,E*), 19.6 (*C*36 *E,E*). ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]THF): δ 4.96 (s, *E,E* isomer), 2.35 (s, *P Z,E* isomer). Elemental analysis ($C_{36}H_{32}NP$, 509.60): Calcd C, 84.84; H, 6.33; N, 2.75; P, 6.08. Found: C, 84.31; H, 6.18; N, 2.75. MS (EI, *m*/*z*): 525 (10) [M + O], 509 (50) [M], 389 (60) [M − $C_8H_{11}N$], 370 (100), 322 (30) [M − L], 183 (100), 118 (60) [$PhNC_2H_3$], 77 (25) [Ph]. IR: 3051 w, 3025 w, 2914 w, 1587 m, 1570 m, 1510 s, 1477 m, 1361 m, 1317 m, 1281 m, 1186 m, 1104 s, 1027 m, 911 m, 806 s, 767 s, 742 vs, 692 vs, 596 m, 557 m, 499 s, 461 m.

Crystal Structure Determinations. The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo K_α radiation. The data were corrected for Lorentz and polarization effects; absorption was taken into account on a semiempirical basis using multiple scans.[12−14] The structures were solved by Direct Methods (SHELXS[15]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97).[15] All hydrogen atoms (with the exception of the methyl groups of C35 and C36 of compound *Z,E*-**3**) were located by difference Fourier synthesis and refined isotropically. All non-hydrogen atoms were refined anisotropically.[15] Crystallographic data as well as structure solution and refinement details are summarized in the Supporting Information. XP (SIEMENS Analytical X-ray Instruments, Inc.) 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.inorgchem.6b00586. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1457771 for *E,E*-**1**, CCDC-1457772 for *Z,E*-**1**, CCDC-1457773 for *Z,E*-**2**, and CCDC-1457774 for *Z,E*-**3**.

NMR spectra and details for the quantum chemical studies (PDF)

Crystallographic data of the crystal structure determinations (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We appreciate the financial support of the Fonds der Chemischen Industrie im Verband der Chemischen Industrie e.V. (FCI/VCI, Frankfurt/Main, Germany). F.M.Y. thanks the

DOI: 10.1021/acs.inorgchem.6b00586
Inorg. Chem. XXXX, XXX, XXX−XXX

German Academic Exchange Service (DAAD, Bonn, Germany) for a generous Ph.D. stipend. The infrastructure of our institute was partially provided by the EU (European Regional Development Fund, EFRE).

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DOI: 10.1021/acs.inorgchem.6b00586
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