Tailored Palladium Catalysts for Selective Synthesis of Conjugated Enynes by Monocarbonylation of 1,3-Diyynes

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Abstract: For the first time, the monoalkoxycarbonylation of easily available 1,3-diyynes to give synthetically useful conjugated enynes has been realized. Key to success was the design and utilization of the new ligand 2,2'-bis(tert-butyl(pyridin-2-yl)phosphanyl)-1,1'-binaphthalene (Neolephos), which permits the palladium-catalyzed selective carbonylation under mild conditions, providing a general preparation of functionalized 1,3-enynes in good-to-high yields with excellent chemoselectivities. Synthetic applications that show the possibilities of this novel methodology include an efficient one-pot synthesis of 4-aryl-4H-pyrans as well as the rapid construction of various heterocyclic, bicyclic, and polycyclic compounds.

Introduction

1,3-Enynes have been recognized as versatile building blocks in organic synthesis, enabling further straightforward transformations for rapid construction of molecular complexity. Interestingly, this structural element also occurs in several natural products and pharmaceuticals. In addition, 1,3-enynes are of general importance for material sciences, specifically polymers. Traditional approaches to this class of compounds include olefination of propargyl aldehydes, dehydration of propargyl alcohols, and mainly metal-catalyzed cross-addition of alkenes. In addition, the transition-metal-catalyzed Sonogashira coupling reaction of alkyynes with vinyl halides and related cross-coupling reactions between terminal organometallic alkyynes and alkenes provide prevalent methodologies for their synthesis. Despite all these remarkable progresses, there is continuous interest in the development of a more efficient and general synthesis of functionalized 1,3-enynes from readily available starting materials.

One of the main driving forces for the advancement of modern organic chemistry is the development of novel catalysts/ligands owing to their key role in controlling the reactivity and selectivity of chemical transformations. Applying transition-metal complexes as catalysts, especially considering the electronic and steric nature of the ligands is crucial, and often enables previously unknown transformations. Notably, for practical purposes often the activity of a given catalyst is the decisive factor for its application. Consequently, the design of new catalysts with both improved activity and selectivity compared with known catalytic systems is essential for the development of useful synthetic methodologies. As representative examples, we recently demonstrated the advantage of specific phosphine ligands with a built-in-base function for palladium-catalyzed alkoxycarbonylation reactions of less-reactive olefins, including hindered tri- and tetra-substituted alkenes. Incorporation of tert-butyl and pyridine substituents on the phosphorous atom of several bidentate phosphate ligands dramatically improved the rate of the nucleophilic attack on the intermediate palladium acyl complex, which can be rate-limiting in these catalytic protocols.

Based on this work, we started a program to investigate the palladium-catalyzed carbonylation of 1,3-diyynes, which are easily available from terminal alkyynes via the Glaser coupling reaction and its variants. Indeed, utilization of the specific ligand 1,1'-ferrocenediyl-bis(tert-butyl)(pyridin-2-yl)-phosphine allowed for the carbonylation to give substituted conjugated dienes. Unfortunately, none of the explored catalyst systems allowed for a selective monocarbonylation that could afford synthetically useful 1,3-enynes. To the best of our knowledge no general catalytic monocarbonylation process of these substrates has been developed so far. Obviously, a key challenge for this transformation is to avoid the generation of double carbonylation products (Scheme 1, a). This challenge could be difficult owing to the similarity between diyne and enyne. Herein, we present a solution for this problem by careful control of the reaction conditions and design of the new ligand L12. A highly selective monocarbonylation of a variety of 1,3-diyynes is possible, affording a precise synthesis of conjugated enynes (Scheme 1, b).

Results and Discussion

In general, for palladium-catalyzed alkoxycarbonylations the choice of ligand is crucial for controlling the selectivity and activity of the overall transformation. Thus, we inves-
tigated the effect of different phosphine ligands in the benchmark reaction of commercially available 1,4-diphenyl-buta-1,3-diyne 1a and n-butanol 2a [40 bar CO, toluene, 1.0 mol% Pd(TFA)2, 4.0 mol% bidentate and 8.0 mol% monodentate phosphines, and PTSA·H2O (p-toluenesulfonic acid monohydrate)], as shown in Scheme 2. To avoid multiple carbonylation reactions, only 1 equivalent of alcohol was used, and the reactions were generally run at room temperature. To our delight, the desired enyne 3aa was obtained in 76% yield when L1 was applied, demonstrating the general feasibility of a monocarbonylation process. In addition, the generation of the double carbonylation product 4aa (3aa/4aa = 87/13) was observed. Unfortunately, the separation of both products was tedious. Thus, we were interested in more selective catalyst systems and tried other bidentate ligands L2–L4 bearing tert-butyl and pyridyl substituents on the phosphorus atom. In the presence of L2, 3aa was afforded in slightly higher yield; however, no improvement of the chemoselectivity was achieved. When using L3 or L4 with a different ligand backbone, the overall yield of carbonylation products was lower, although high selectivity for 3aa was realized. Other state-of-the-art ligands that are commonly used in carbonylations, such as 4,5-bis(diphenylphosphino)-9,9-dimethyl-xanthene (Xantphos, L5),[17] 1,3-bis(diphenylphosphino)propane (dppp, L6),[18] 1,4-bis(diphenylphosphino)butane (dppb, L7),[19] 1,2-bis(di-tert-butylphosphanyl-yl)-methylbenzene (dppbx, L8),[20] 2-diphenylphosphinopyridine (L9),[21] and di(1-adamantyl)-n-butyl-phosphine (BuPAd2, L10),[22] did not give the desired product in more than 40% yield. Interestingly, when using racemic 2,2’-bis(diphenylphosphanyl)-1,1’-binaphthalene (L11, BINAP)[23,24] as a ligand, 3aa was obtained in 74% yield and more surprisingly the chemoselectivity was also increased to 95/5. Comparing L6 with L3 and L7 with L4, as well as L8 with L2, demonstrates the superior behavior of the tert-butyl-2-pyridylphosphino group in the respective ligands. Consequently, we prepared the analogous ligand L12, which to the best of our knowledge had never been synthesized before. Gratifyingly, by applying L12 the desired monocarbonylation product 3aa was obtained in 93% yield with 99/1 chemoselectivity. It should be noted that L12 consists of a mixture of stereoisomers, which could be used directly in this reaction because the different stereoisomers have no significant influence in this transformation (for more details, see the Supporting Information).

To improve the benchmark reaction further, we evaluated the influence of critical reaction parameters in the presence of L12. As shown in Table 1, no reaction occurred without acid or with weak acid (Table 1, entries 1 and 2). Even trifluoroacetic acid gave only trace amounts of 3aa, whereas pyridine-2-sulfonic acid afforded the desired product in 12% yield (Table 1, entries 3 and 4). Interestingly, by using camphorsulfonic acid (CSA), the preferred product 3aa could be obtained in 93% yield with 99/1 chemoselectivity. The data for the benchmark reaction are summarized in Table 1.
Table 1: Pd-catalyzed monocarbonylation of 1,4-diphenylbuta-1,3-dyne: Investigation of reaction conditions.[3]

| Entry | [Pd] | Acid | 3a/4a | Yield of 3a [%] |
|-------|------|------|-------|----------------|
| 1     | Pd(TFA)₂ | no acid | – | 0 |
| 2     | Pd(TFA)₂ | HOAc | – | 0 |
| 3     | Pd(TFA)₂ | TFA | – | < 5 |
| 4     | Pd(TFA)₂ | 2-PySO₃H | 99/1 | 12 |
| 5     | Pd(TFA)₂ | HTf | 99/1 | 45 |
| 6     | Pd(TFA)₂ | PTSA-H₂O | 99/1 | 93 |
| 7     | Pd(TFA)₂ | (+)-CSA | 99/1 | 96 |
| 8     | Pd(TFA)₂ | (+)-CSA | 99/1 | 68 |
| 9     | Pd(acac)₂ | (+)-CSA | 99/1 | 77 |
| 10    | PdCl₂ | (+)-CSA | – | 0 |
| 11    | Pd(dba)₃ | (+)-CSA | 99/1 | 25 |
| 12    | Pd(OAc)₃ | (+)-CSA | 99/1 | 88 |
| 13    | Pd(OAc)₂ | (+)-CSA (1.0/4.0/mol) | 99/1 | 97 (94) |
| 14    | Pd(OAc)₂ | (+)-CSA | 99/1 | 97 |
| 15    | Pd(OAc)₂ | (+)-CSA | 99/1 | 97 |

[a] Unless otherwise noted, all reactions were performed under 40 atm CO at room temperature for 20 h in the presence of 1a (0.25 mmol), 2a [0.25 mmol], [Pd] (1.0 mol% in terms of palladium atom), L12 (4.0 mol%), acid (8.0 mol%) in toluene (1.0 mL). The yield and chemoselectivity (3a/4a) were determined by GC analysis. [b] The reaction time was 4 h. [c] 0.5 mmol nBuOH was used. [d] 40°C. [e] Yield of isolate product.

achieved in 96% yield with excellent chemoselectivity (Table 1, entry 6). It should be noted that using CSA as the co-catalyst also improved the solubility of catalysts. Besides, the palladium precursor had a significant influence on the productivity and palladium acetate was found to be the most active metal salt giving 3a in 88% (4 h) and 97% (20 h) yield (Table 1, entries 12 and 13). Notably, smooth transformations with excellent yields and selectivities were also observed in the presence of an excess amount of 1-butanol or at higher temperature (Table 1, entries 14 and 15), which demonstrated the preferred selectivity for monocarbonylation.

To understand the behavior of L12 in controlling the chemoselectivity, we studied the kinetic process of the alkoxy carbonylation of 1,4-diphenylbuta-1,3-dyne 1a with n-butanol (1.0 equiv). As shown in Figure 1(a), the yield of desired product 3aa increased gradually and the starting material 1a was fully converted after 12 hours. Over the course of the reaction, the double carbonylation product was not detected at all. To get more insight into the activity and selectivity of ligand L12, the reaction was also performed at room temperature with a large excess of methanol (solvent). As depicted in Figure 1(b), the monocarbonylation product 3ab was generated in high chemoselectivity over 25 hours, and only after that time the second carbonylation occurred at very low rate. Even after 3 days, the double carbonylation product was observed only in 10% distribution, showing the pronounced rate differences between the first and second carbonylation step.

On the basis of these results and our previous work on the mechanism of alkoxy carbonylation using ligands L1–L4,[12–14], as well as the mechanistic studies by Cole-Hamilton, Drent, and Sparkes,[24] we propose the following catalytic cycle for ligand L12 [Figure 1(c)]. Initially, the stable Pd⁰ salt is reduced in situ to Pd¹ in the presence of an excess amount of phosphine ligands,[25] followed by a protonation process to afford the active complex A. It is likely that this palladium hydride species is in equilibrium with the N-protonated pyridinium complex.[13] Subsequently, N-coordination of one carbon–carbon triple bond to the metal center occurs, followed by the insertion of the alkyno into the palladium hydride bond, affording the alkenyl–Pd intermediate B. After CO insertion, the complex C is formed and N-assisted methanolysis of intermediate C via transition state D provides the desired monocarbonylation product 3ab and regenerates the active palladium hydride species, to finish cycle I. On the other hand, the carbon–carbon triple bond of 3ab might coordinate to the active palladium hydride species again and insertion of the triple bond will give intermediate E, which undergoes another CO insertion process to afford acyl palladium species F. Finally, N-assisted methanolysis affords the undesired product 4ab and again regenerates palladium hydride species A to complete cycle II.

Following our original goal to develop a general protocol for the synthesis of functionalized 1,3-enzymes, we started to explore the substrate scope. With the optimized reaction conditions in hand (for details see the Supporting Information), we studied the monoalkoxy carbonylation of 30 different 1,3-diynes by using Pd(OAc)₂/L12(+)–CSA (1.0/4.0/8.0 mol%) as the catalyst. As shown in Table 2, a variety of substrates, including symmetric aromatic and aliphatic, and more importantly also non-symmetric substrates, bearing a range of functional groups, are transformed into the corresponding conjugated enynes in good-to-excellent yields (53–95%). Notably, in all these cases high chemoselectivities (mono/di = 99/1) and exclusive generation of the E-stereoisomers was observed. Aromatic 1,3-diynes 1a–i with either electron-donating (OMe, Me, tBu) or electron-withdrawing (F, CF₃) substituents on the phenyl ring provided the corresponding products 3aa–3ui in high yields (83–95%) and excellent selectivity under very mild conditions (room temperature). Substituents in the ortho-position of the phenyl ring have a significant influence on both reactivity and selectivity of this reaction. As an example, the 1,4-di-ortho-tolylbuta-1,3-dyne 1k gave 3ka in 83% yield at 70°C with 86/14 regioselectivity. Pleasingly, the thiofuran-substituted substrate was well tolerated by the catalyst; thus, 3la was obtained in 93% yield. Next, we investigated the reactivity of aliphatic 1,3-diynes. Gratifyingly, the palladium-catalyzed monoalkoxy carbonylation of various substrates proceeded selectively, affording the corresponding carbynlative products in good yields and selectivities. It should be noted that no other side product was observed in all these cases, although the desired products may undergo isomerization processes. The simple 1,3-diynes 1m–1o and the cyclohexyl- and cyclopentyi-substituted 1,3-diynes 1p and 1q, also gave the preferred products in 55–90% yield and high selectivity under mild conditions.

Furthermore, substrates bearing substituents such as chloride, cyano, ester, and trimethylsilyl also smoothly under-
went monocarbonylation and gave the desired products $3_{wa}$ in 74–84\% yields. Next, the scope of non-symmetric 1,3-diynes, which are more challenging substrates from the viewpoint of regioselectivity, was examined. As shown in Table 2, reaction of the non-functionalized 1-phenyl-4-hexyl-1,3-butadiyne $1_x$ gave selectively the monocarbonylative product, albeit as a mixture of two regioisomers with 57/43 selectivity. Although in this case the carbonylation proceeded slightly further at the phenyl-substituted alkyne group, interestingly, $1_y$, $1_z$, and $5_a$ bearing chloride, cyano, and amide end groups led to regioisomers $3_y a$ (44/56), $3_z a$ (36/64), and $5_{aa}$ (25/75), respectively, as the main products. Nevertheless, depending on the substrate the regioselectivity for the monocarbonylation can also be very high, allowing the synthesis of interesting functionalized building blocks. More specifically, propargyl ester/amide-derived 1,3-diynes $5_b$, $5_c$, $5_d$, and $5_e$, which are often sensitive to palladium catalysis, worked particularly well, affording the corresponding products with excellent regioselectivities (> 20/1). Moreover, carbonylation of unsymmetrical 1,3-diyne $5_f$ preferentially occurred at the phenyl-substituted triple bond, affording product $5_{fa}$ regioselectively (92/8) in 80\% yield.

Next, we examined the general scope of this monocarbonylation process with respect to the reactivity of alcohols. Thus, a variety of simple primary aliphatic alcohols, including some functionalized derivatives ($2_f$ and $2_g$), were tested under the optimal reaction conditions. As shown in Table 3, the corresponding esters ($3_{ab}$–$3_{a h}$) were generated in high yields (86–94\%) with chemoselectivities of > 99/1. Moreover, less reactive secondary alcohols underwent this reaction smoothly in very good yields and selectivities ($3_{aj}$–$3_{al}$, 82–90\% yields, > 99/1 chemoselectivities). Surprisingly, even tert-butanol as an example of a tertiary alcohol was suitable for this transformation to give $3_{am}$. Furthermore, alcohols $2_n$–$2_p$ containing heterocyclic rings proved to be viable substrates and gave the corresponding products $3_{an}$–
3ap in 91–96% yields with >99/1 selectivities. To our surprise, this transformation could also be performed in the presence of alkene (2q) or isolated alkynes (2r and 2s) giving the highly functionalized carbonylative products 3aq–3as in 60–90% yields; thus, demonstrating interesting chemoselectivity. Notably, diverse alcohols can be used in this transformation, also highlighting the substrate scope of this protocol and its potential utility in organic synthesis (Table 3).

More specifically, constituents of cosmetic fragrances, such as (Z)-Nerol and (R)-Nopol, bearing carbon/C0 carbon double bonds, gave the corresponding products 6a and 6b in 90 and 76% yield, respectively. Moreover, (R)-Borneol, a traditional Chinese medicine that is also the component of many essential oils and natural insect repellent, and (–)-Menthol, which is widely used for its medicinal value, furnished the carbonylative products 6c and 6d in 70–83% yield. Applying L-serine and α-D-galactopyranose derivatives as other representative examples of biologically relevant molecules afforded the desired products 6e and 6f in 78–85% yield. Furthermore, cholesterol, which is an essential structural component of all animal cells and is required to maintain the structural integrity of membranes, was identified to be a good substrate in this transformation. Similarly, steroid hormones such as Testosterone, Pregnenolone, and Androstanelone participated in this transformation efficiently to provide the modified bio-active compounds 6h–6j in high yields.

Table 2: Pd-catalyzed monocarbonylation of 1,3-diynes with n-butanol: Substrate scope.\[a\]

| R1–R2 | \( \text{CO}_2\text{Bu} \) | Pd(OAc)\(_2\) (1.0 mol%), L12 (4.0 mol%) | (+)-CSA (8.0 mol%) | toluene (40 bar), T, 20 h | R1 | \( \text{CO}_2\text{Bu} \) |
|--------|-----------------|---------------------------------|-----------------|-------------------|--------|-----------------|
| 3aa-3wa, 5aa-5fa | 1a-1z, 5a-6f, 2a (1.0 equiv.) | \( \text{CO}_2\text{Bu} \) | \( \text{CO}_2\text{Bu} \) | 3aa, 23 ℃, 83% (>99/1); 3ba, R = Me, 23 ℃, 86% (>99/1); 3ca, R = Bu, 23 ℃, 91% (>99/1); 3da, R = OMe, 23 ℃, 90% (>99/1); 3ea, R = F, 23 ℃, 92% (>99/1); 3fa, R = CF\(_3\), 23 ℃, 90% (>99/1); 3ga, 23 ℃, 83% (>99/1); 3ha, R = Me, 23 ℃, 76% (>99/1); 3ia, R = CO\(_2\)Me, 40 ℃, 81% (>99/1); 3ja, R = Cl, 40 ℃, 74% (>99/1); 3ka, R = CN, 40 ℃, 75% (>99/1); 3la, 23 ℃, 88% (>99/1); 3ma, R = Me, 23 ℃, 76% (>99/1); 3na, R = CH\(_3\), 23 ℃, 75% (>99/1); 3oa, R = C\(_6\)H\(_5\), 23 ℃, 77% (>99/1); 3pa, R = Cy, 40 ℃, 86% (>99/1); 3qa, 23 ℃, 90% (>99/1); 3ra, R = Ph, 40 ℃, 88% (>99/1); 3sa, R = CO\(_2\)Me, 40 ℃, 81% (>99/1); 3ta, R = Cl, 40 ℃, 74% (>99/1); 3ua, R = CN, 40 ℃, 75% (>99/1); 3va, 40 ℃, 76% (>99/1); 3wa, 40 ℃, 70% (>99/1) regioselectivity (1/2): 57/43 3xa, 40 ℃, 82% (>99/1) regioselectivity (2/1): 82/18 3za, 40 ℃, 82% (>99/1) regioselectivity (2/1): 83/17 5aa, 40 ℃, 85% (>99/1) regioselectivity (2/1): 75/25 5ba, 40 ℃, 53% (>99/1) regioselectivity (2/1): 20/1 5ca, 40 ℃, 60% (>99/1) regioselectivity (2/1): 20/1 5da, 40 ℃, 76% (>99/1) regioselectivity (2/1): 20/1 5ea, 60 ℃, 85% (>99/1) regioselectivity (2/1): 20/1 5fa, 50 ℃, 80% (>99/1) regioselectivity (2/1): 92/8

[a] Unless otherwise noted, all reactions were performed under 40 atm CO for 20 h in the presence of 1 (0.25 mmol), 2a (0.25 mmol), Pd(OAc)\(_2\) (1.0 mol%, 0.56 mg), L12 (4.0 mol%, 5.84 mg), (+)-CSA (8.0 mol%, 4.6 mg) in toluene (1.0 mL) at specified temperature. The yields are those of product isolated by column chromatography. The chemoselectivity in brackets (mono/di) were determined by GC analysis. The regioselectivity of 3xa–3za and 5aa–5fa were determined by \( ^1 \)H NMR analysis of the crude products. [b] 2/8/16 mol% of Pd/L12/(+)-CSA was used.
structure of 6i was confirmed further by X-ray diffraction. Finally, Isosorbide, a diol that is used to treat brain edema and glaucoma, was also compatible in this protocol, producing 6k in 83% yield.

To demonstrate the usefulness of the resulting products as intermediates in organic synthesis, we performed the effective synthesis of several 4-phenyl-4H-pyrans 7a–7j in 71–85% yield directly from different (non)symmetrical 1,3-dynes.
Scheme 3. Gram-scale synthesis of 3aa, 3wa, and 5fa and their further synthetic transformations. Reagents and conditions: (i) MeNH2, HOH·HCl, trimethylamine, DCE, 0°C for 10 h, then rt for 10 h; (ii) NH2NH2·H2O, K2CO3, DMA, 40°C, air, 24 h. (iii) Diethyl aminoformylmalonate hydrochloride, DBU, DMF, 40°C, 12 h. (iv) Cyclohexanone, pyrrolidine, InCl3, 4Å molecular sieves, DCE, 80°C, 20 h. [a] rt, 20 h.

Advantageously, the presented methodology can be easily scaled up as shown by the gram-scale synthesis of 3aa, 3wa, and 5fa using 5.0 mmol of 1,4-diphenylbuta-1,3-diyne 1a, 1,4-bis(trimethylsilyl)buta-1,3-diyne 1w, and trimethyl(phenylbuta-1,3-diyne-1-yl)silane 5 under standard reaction conditions, affording 3aa, 3wa, and 5fa in 87, 91, and 78% yield, respectively, [Scheme 3, (1)].

As mentioned in the introduction, 1,3-enynes are important synthons in organic chemistry. With this particular carbonylation methodology available, we are able to provide a diverse array of new building blocks. Indeed, except for two compounds (3ab and 3ac) all the other prepared products were synthesized for the first time, also demonstrating the novelty of our approach. To showcase the usefulness of these now easily accessible building blocks, various follow-up transformations were conducted by using 3aa or 5fa as the starting material (Scheme 3). For example, tri-substituted 2,3-dihydroisoxazoles 8a and 8b were obtained in 86–87% yield in the presence of N-methyl hydroxylamine hydrochloride and TEA (triethylamine). The similar reaction was performed by using hydrazine and K2CO3, affording pyrazole compound 9a in 82% yield. Interestingly, when using 5fa under the same conditions, the trimethylsilyl group was removed and product 9b was afforded in 80% yield. Treatment of 3aa with diethyl ammonalane hydrochloride and DBU provided the 2,3-dihydro-1H-pyrrrole 10a via a formal [3+2] cycloaddition. Similarly, 10b was produced in 84% yield from 5fa under slightly modified conditions and again the trimethylsilyl group was removed. Moreover, the bicyclo[3.3.1]alkenones 11a and 11b, which are present in numerous bioactive natural products, were also achieved by In-catalyzed intramolecular α,α’-amellation of enamine with 3aa and 5fa.[30] Finally, the facile synthesis of angularly fused polycycles 12[31] illustrated the diverse possibilities of the prepared conjugated enynes for the construction of complex molecules.

Conclusion

In summary, we have developed the first general monooxycarbonylation of 1,3-dienes with aliphatic alcohols to produce a variety of synthetically useful conjugated 1,3-enynes with excellent chemoselectivity. Key to success is the design of a tailored palladium catalyst based on the new ligand Neolephos, allowing efficient monocarbonylation. Notably, most of the synthesized products are new, because the preparation of this scaffold was previously not an easy task. The synthetic utility of our protocol was showcased further in the rapid construction of various heterocyclic compounds.
bicyclic, and polycyclic compounds from alkynes in only three steps (alkyne→1,3-diyne→1,3-enyne→heterocycles). We believe this procedure, as well as the new ligand design, will complement the available toolbox of carbylonylation reactions.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: conjugated enynes - monocarbylonylation - P ligands - palladium - selectivity

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