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Palladium-Catalysed Reductive [5+1] Cycloaddition of 3-Acetoxy-1,4-enynes with CO: Access to Phenols Enabled by Hydrosilanes

Li-Jun Wu, Ren-Jie Song*, Shenglian Luo and Jin-Heng Li*

Dedicated to Professor Xiyan Lu on the occasion of his 90th birthday

Abstract: A new palladium-catalysed reductive [5+1] cycloaddition of 3-acetoxy-1,4-enynes with CO enabled by hydrosilanes is developed for producing valuable functionalized phenols. This methodology employs hydrosilanes as the external functional reagents to fulfil the [5+1] carbonylative benzannulation, and is featured as a conceptually and mechanistically novel carbonylative cycloaddition route to construct substituted phenols through the formation of four new chemical bonds with excellent functional group tolerance.

The cycloaddition reaction is a central theme that has become one of the most powerful and straightforward platforms to build various cyclic structural systems in synthesis.[1,2] Among these diverse functionality capable of cycloaddition strategies, transition-metal-catalyzed carbonylative benzannulation strategy[1,2] represents a unique technology that has long intrigued the synthesis community because it employs economical carbon monoxide as a one-carbon building block to de novo construct the important phenol ring systems found in natural products, pharmaceuticals and functional materials.[3] Traditional carbonylative benzannulation methods usually rely on the formation of Fischer carbenes using a stoichiometric amount of transition metals (e.g. chromium and iron).[4] Over the past two decade, many efficient transition-metal-catalyzed carbonylative benzannulation alternatives, including [3+2+1],[5] [5+1][6] and other elegant cycloaddition modes,[7] have been established for transformations of unsaturated hydrocarbons and CO into functionalized phenol derivatives. Generally, these catalytic versions are initiated by either strain-ring opening or intramolecular nucleophilic addition, with the majority of current catalytic systems concerning rhodium salts.[2,5-7]

Compared to the strain-ring opening strategy,[5a-b,5f-g,6f-i,6k,6p] the nucleophilic addition strategy[5c-e,6a-e,6j,6l-n,6o] appears to be superior and more practical owning to the easily accessible substrates and the resulting more functionalized products.[2,5-7] However, such events are all limited to the use of the inherent nucleophilic groups, and challenges in the preparation of reaction partners have restricted this strategy. To the best of our knowledge, reports of the external functional group addition strategy for enabling the carbonylative benzannulation have yet reported. In 2012, the group of Fukuyama, Ryu, Fensterbank and Malacria[6a-b] first reported a $[RhCl(CO)_2]_2$-catalyzed [5+1] cycloaddition between 1,4-enyne esters with CO toward resorcinols by 1,2-acyloxy migration (Scheme 1a). However, the [5+1] cycloaddition mode is restricted to terminal alkynes and suffers from the requirement of high pressure (50-80 atm of CO). Tang group[6j,6m] has employed the inherent amido nucleophiles to achieve a new [5+1] carbonylative benzannulation under 1 atm CO conditions (Scheme 1a); this method is applicable to a wide range of 3-aminophenyl-containing 3-hydroxy-1,4-enynes as the new 5-carbon components, but is only sensitive to Rh catalysts. We envisioned that an external functional group could coordinate with an active metal species to achieve the carbonylative benzannulation upon addition across a C-C unsaturated bond in the 1,4-enyne, which would offer a new robust annulation mode for accessing diverse substituted phenols from the same unsaturated hydrocarbon synthon.

Herein, we report a new palladium-catalysed reductive [5+1] cycloaddition of 3-acetoxy-1,4-enynes toward substituted phenols when combined with both CO and hydrosilanes[8] (Scheme 1b). This reaction allows the formation of four new chemical bonds via a new initiation mode that utilizes hydrosilanes as the external functional reagents to achieve this event, and represents a conceptually and mechanistically novel carbonylative benzannulation method using a reductive Pd catalysis strategy.[8]

Initial studies chose three components, namely, 1,5-diphenylpent-1-en-4-yn-3-yl acetate (**1a**), carbon monoxide (CO) and triethylsilane (**2a**), for optimization of the [5+1] cycloaddition reaction conditions (Table 1). Exposure of 1,4-enyne **1a** (0.2 or even 1 mmol) to 1 atm CO and 1.2 equiv silane **2a**, 10 mol% $PdCl_2$ and 20 mol% PPh_3 in $PhCF_3$ at 100 °C for 6-8 h led to the desired product **3a** in high yield (entry 1). The results showed that Pd catalyst was needed to execute the reaction and 10 mol% $PdCl_2$ proved to be the best option (entries 1-8). While the reaction could not occur in the absence of Pd catalysts (entry 2), adding the $PdCl_2$ loading to 5 mol% sharply enhanced the yield of **3a** to 67% (entry 3) and raising to 10 mol% led to the highest efficiency (entry 1). Further increasing the $PdCl_2$ loading to 15 mol% still remained excellently effective, but had no further improvement of yield (entry 4). The other Pd catalysts (entries 5-8), including $Pd(OAc)_2$, $Pd(PPh_3)_2Cl_2$, $Pd(dba)_2$ and $Pd(PPh_3)_4$, were inferior to $PdCl_2$. Using ligands could improve the reactivity, as without ligands **3a** was assembled in 9% yield. Other ligands,

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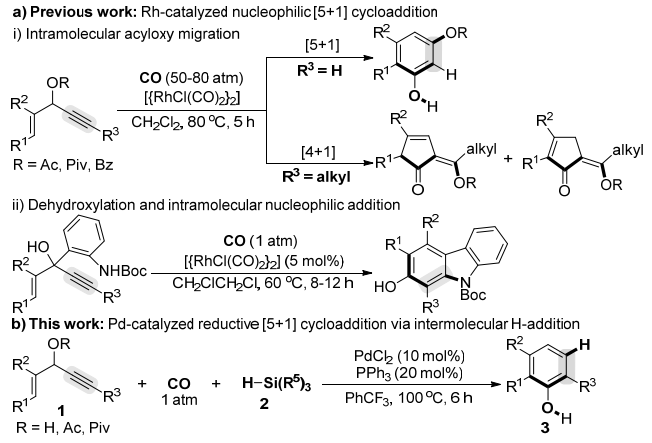
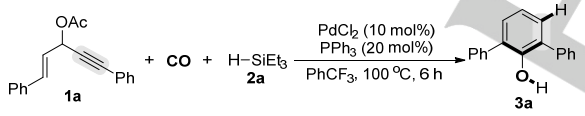


Scheme 1. Driven [5+1] cycloaddition of 3-acetoxy-1,4-enynes with CO. Ac = acetoxy. Piv = pivaloyl. Bz = benzoyl. Boc = *tert*-butoxycarbonyl.

such as P(*o*-tol)$_3$, P(*t*-Bu)$_3$ and 1,2-bis(diphenylphosphino)-ethane (dppe), were less effective than PPh_3 (entries 10-12). Two other solvents, toluene and 1,4-dioxane, accommodate to the [5+1] annulation, albeit slightly diminishing yields (entries 13 and 14). Brief screening of the reaction temperatures indicated that lowering (80 °C) or raising (120 °C) the temperature each had a negative effect, but still gave fairly good yields (entries 15 and 16). Notably, two alternative hydrosilanes, triisopropylsilane (**2b**) and triphenylsilane (**2c**), exhibited high reactivity (entries 17 and 18), and the latter was preferred. However, tetraethylsilane (**2d**) without the free Si-H bond had no reactivity (entry 19).

Table 1. Screening of optimal reaction conditions[a]



Entry	Variation from the Standard Conditions	Isolated Yield [%]
1	none	85/82[b]
2	without $PdCl_2$	0
3	$PdCl_2$ (5 mol%)	67
4	$PdCl_2$ (15 mol%)	83
5	$Pd(OAc)_2$ instead of $PdCl_2$	33
6	$Pd(PPh_3)_2Cl_2$ instead of $PdCl_2$	46
7	$Pd(dba)_2$ instead of $PdCl_2$	21
8	$Pd(PPh_3)_4$ instead of $PdCl_2$	54
9	without PPh_3	9
10	P(*o*-tol)$_3$ instead of PPh_3	63
11	P(*t*-Bu)$_3$ instead of PPh_3	15
12	dppe instead of PPh_3	12
13	toluene instead of $PhCF_3$	78
14	1,4-dioxane instead of $PhCF_3$	71
15	at 80 °C	80
16	at 120 °C	73
17	$HSi(i\text{-}Pr)_3$ (**2b**) instead of $HSi(Et)_3$ (**2a**)	86
18[c]	$HSi(Ph)_3$ (**2c**) instead of $HSi(Et)_3$ (**2a**)	90/91[b]
19	$Si(Et)_4$ (**2d**) instead of $HSi(Et)_3$ (**2a**)	0

[a] Reaction conditions: **1a** (0.2 mmol), CO (1 atm), **2a** (1.2 equiv), $PdCl_2$ (10 mol%), PPh_3 (20 mol%), $PhCF_3$ (2 mL), 100 °C, and 6 h. [b] **1a** (1 mmol) and $PhCF_3$ (4 mL) for 8 h. [c] $AcOSi(Ph)_3$ (**4**) was observed by GC-MS analysis. tol = tolyl. dba = dibenzylideneacetone.

Having establishing the optimal reaction conditions, we then assessed the scope of this reductive [5+1] annulation protocol with regard to 3-acetoxy-1,4-enynes **1** (Table 2 and Scheme 2). In the presence of CO, Ph_3SiH **2a**, $PdCl_2$ and PPh_3, a wide range of aryl and alkyl substituents on the alkene moiety of 3-acetoxy-1,4-enynes **1** were tolerated well (**3b-i**), although their electronic properties and positions both affected the reactivity. While enynes **1b-c** having an electron-rich aryl group (e.g. *p*-MeC_6H_4 and *p*-$MeOC_6H_4$) delivered **3b-c**, respectively, in excellent yields, enynes **1d-e** with a weak (*p*-ClC_6H_4) or a strong (*p*-$CF_3C_6H_4$) electron-deficient aryl group tendered **3d-e** in slightly decreased yields. This technology is efficient with *m*-$MeOC_6H_4$-substituted enyne **1f** (88% yield; **3f**), but moderate with *o*-$MeOC_6H_4$-substituted (*E*)- or (*Z*)-enynes **1g** and **1g'** (71% or 70% yields; **3g**) that suggests a dynamical control approach. An alkyl group or a phenyl group at the terminal or internal alkene moiety accommodated this reaction, giving **3h** and **3j-k** in good yields. Terminal alkene **1i** also succeeded in accessing **3i**. Surprisingly, other germinal-disubsituted terminal alkene **1l** gave 10% of **3l** and 42% 2,4-dien-1-one **3l'**, suggesting addition of CO through two C-C π-bond cleavage prior to lose of OAc/ isomerization. However, a methyl group on 3 position to 3-acetoxy-1,4-enyne **1m** had no reactivity (**3m**), probably due to its steric hindrance leading to a slow oxidative addition into the allyl C-O bond. Attempt to use of phenyl ring instead of the C=C bond is failed (**3n**), whereas furan ring [1-(furan-3-yl)-3-phenylprop-2-yn-1-yl acetate **1o**] led to **3o** in good yield. Yet, annulation of enyne **1o** can not executed without hydrosilanes **2**.

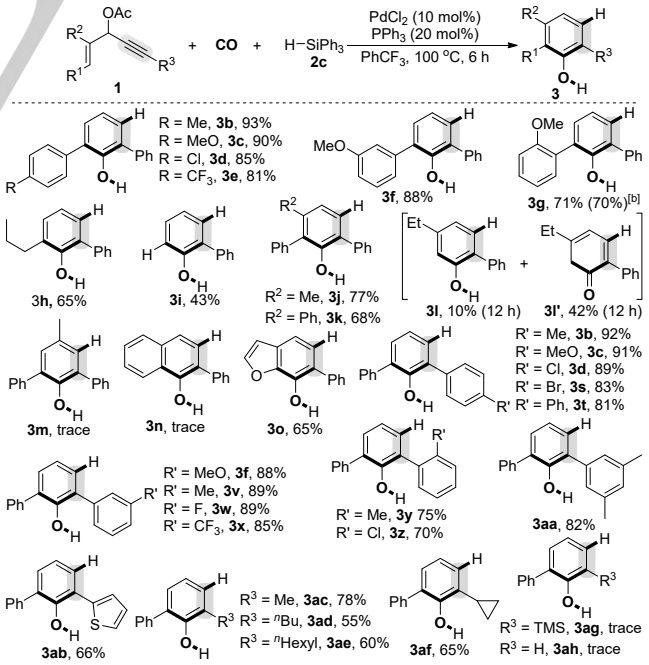


Table 2. Variation of the 3-acetoxy-1,4-enynes (**1**). [a] Reaction conditions: see Table 1. [b] (*E*)-isomer gave 71% yield and (*Z*)-isomer afforded 70% yield. TMS = trimethylsilyl.

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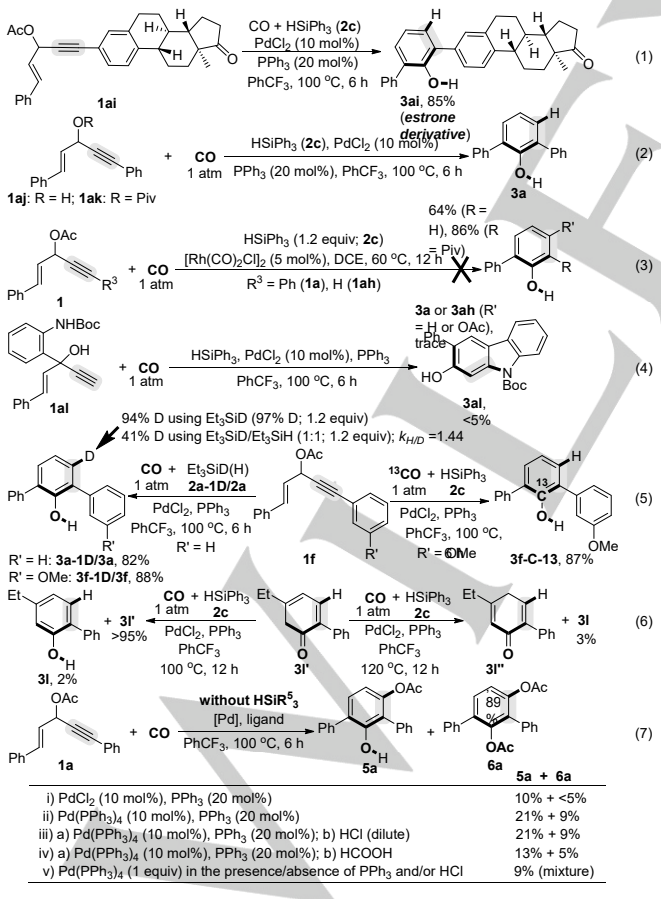
The substitution effect at the terminal alkyne moiety was next examined. Tolerated on the phenyl ring at the terminal alkyne moiety are a wide range of substituents, including *p*-Me (**1p**), *p*-MeO (**1q**), *p*-Cl (**1r**), *p*-Br (**1s**), *p*-Ph (**1t**), *m*-MeO (**1u**), *m*-Me (**1v**), *m*-F (**1w**), *m*-CF_3 (**1x**), *o*-Me (**1y**), *o*-Cl (**1z**) and 3,5-diMe (**1aa**), albeit slightly affecting the yields by substituent electronic properties and positions (**3b-d**, **3s-t**, **3f**, and **3v-aa**). Importantly, halogen atoms, such as Cl, Br and F, remain untouched, thereby offering the subsequent modification potential (**3d, 3s**, **3w** and **3z**). It was noted that using thiophen-2-yl-substituted enyne **1ab** smoothly enabled the formation of **3ab** in 66% yield. In addition, the alkyne system possessing a bioactive estrone analogue group **1ai** succeeded in the construction of **3ai** that comprises both estrone and phenol groups [Eq (1); Scheme 2].[9] Pleasingly, enynes **1ac-af** with a alkyl group (e.g. Me, *n*-Bu, *n*-hexyl and *c*-propyl) at the terminal alkyne were also competent to access **3ac-af**. Unfortunately, TMS-containing alkyne **1ag** and terminal alkyne **1ah** and was inert (**3ag-ah**). This is in contrast to the previous reported Rh-catalyzed [5+2] annulation *via* nucleophilic addition, implying that this current Pd catalysis includes a distinctively different mechanism from these precedents.[2,6]

Moreover, two other enynes **1aj-ak**, in which using a OH or a OPiv group replaced the 3-OAc group, were highly reactive to separately assemble **3a** under the current optimal conditions [Eq (2); Scheme 2]. Acetates **1a** and **1ah** were not amenable to the reported highly active Rh catalyst[6j] even in the presence of

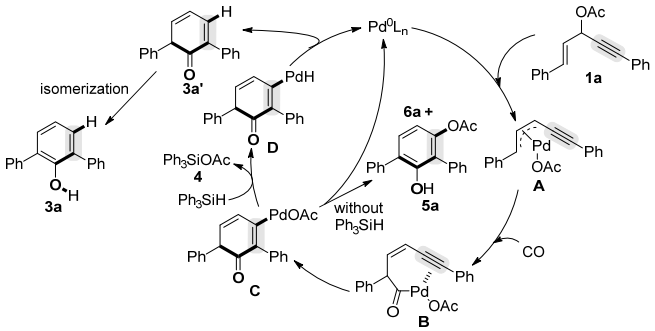


Scheme 2. Cycloaddition of the other enynes (**1**) and control experiments.

Ph_3SiH [Eq (3)]. To further understand the mechanism, (2-(3-hydroxy-1-phenylpent-1-en-4-yn-3-yl)phenyl)-carbamate **1al**, which is an effective 5-carbon component under the Tang conditions,[6j] was prepared to react CO, Ph_3SiH **2a**, $PdCl_2$ and PPh_3, but <5% yield of **3al** was detected [Eq (4)]. The deuterium-labelled reactions with Et_3SiD **2a-1D** showed that this hydrogen atom was entirely from silanes [Eq (5 left)]. The reaction with ^{13}CO further confirmed the regioselectivity of the carbonylation step [Eq (5 right)]. Product **3l'** could be slowly converted into the desired product **3l** at 100 °C, but a higher temperature (120 °C) led to the other isomer **3l''** [Eq (6)]. These results indicate that the cyclohexa-2,4-dien-1-one unit may be a key intermediate in the current reaction, and both the electron and substitution effect makes **3l**' more stable than **3l**. Notably, a mixture of OAc-migration products **5a** and **6a**, were obtained in the absence of hydrosilanes **2** [Eq (7) and Scheme S1 in Supporting Information (SI)].

Consequently, the possible mechanism for this reductive [5+1] carbonylative benzannulation protocol was depicted in Scheme 3.[1,2,5-8] Initially, oxidative addition of the active Pd(0) species with the highly activated allyl acetate **1a** affords the allyl-Pd(II) complexes **A** (also supported by the results of **3n-o**; Table 2).[10] Carbonylation of the complexes **A** with CO at the benzylic position delivers the acyl Pd(II) intermediate **B**, which would sequential undergo carbopalladation across the inherent C≡C bond in the perfect geometry to give the vinyl-Pd(II)-possessing six-membered carbocyclic structure **C**. Reaction of the intermediate **C** with $HSiPh_3$ **2c** generates the Pd^{II} hydride species **D**[8n] (supported by [Eq (5)] and Scheme S1 in SI)[8] and Ph_3SiOAc **4**, followed by reductive elimination of the intermediate **D** offer the intermediate **3a'** and regenerates the active Pd(0) species. Finally, isomerization of the intermediate **3a'** leads to the desired product **3a**.

In the absence of the hydrosilane **2** reductive elimination and isomerization of the intermediate **C** offer the OAc-migration products **5a** and **6a**, albeit with lower efficiency [Eq (7)].



Scheme 3. Possible Reaction Mechanism.

In summary, we have disclosed the first palladium-catalyzed reductive [5+1] carbonylative benzannulation of 3-acetoxy-1,4-enynes with CO and hydrosilanes, in which hydrosilanes served as the external functional reagents are proposed to reductive elimination of the vinyl-Pd species to access the cyclohexa-2,4-dien-1-one unit. This reaction employs a reductive Pd catalysis

strategy to enable the formation of four new chemical bonds through the generation of allylpalladation of the allyl acetate moiety and reductive annulation with CO cascades, which features selectivity for 3-acetoxy-1,4-enynes possessing both the alkene and internal alkyne systems and excellent tolerance of various functional groups. Importantly, additional highlights include facile incorporation of a phenol unit into the bioactive structural systems. Current efforts to further study on utility of this chemistry are underway.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: palladium • carbonylative benzannulation • enynes • hydrosilanes • phenols

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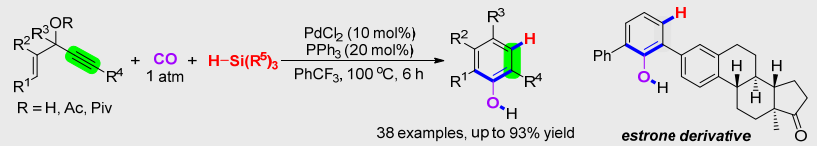

L.-J. Wu, R.-J. Song, S. Luo, and J.-H. Li**

Page No. – Page No.

Palladium-Catalysed Reductive [5+1] Cycloaddition of 3-Acetoxy-1,4-enynes with CO: Access to Phenols Enabled by Hydrosilanes

Employing a reductive Pd catalysis as a new initiation mode enables a new [5+1] carbonylative benzannulation of 3-acetoxy-1,4-enynes with CO and hydrosilanes. This reaction is externally driven by hydrosilanes to fulfil the [5+1] carbonylative benzannulation, and represents a straightforward and practical access to functionalized phenols with excellent functional group tolerance and high selectivity.