

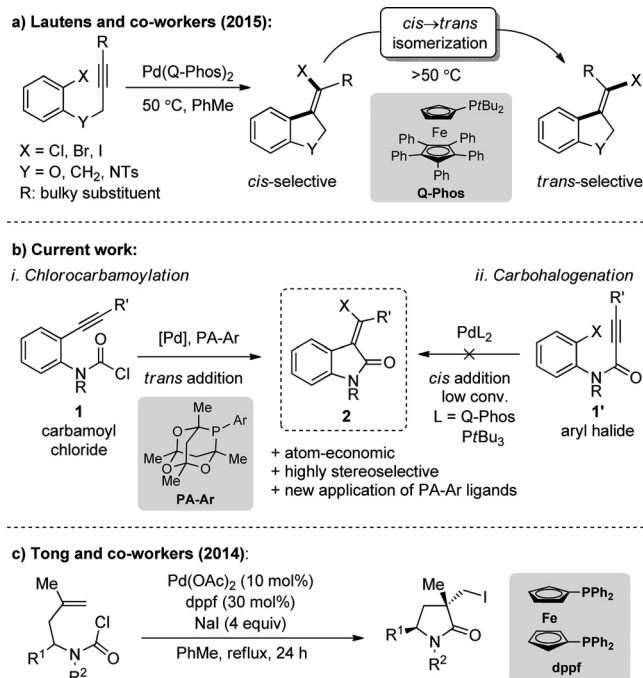
An Exclusively *trans*-Selective Chlorocarbamoylation of Alkynes Enabled by a Palladium/Phosphaadamantane Catalyst

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Abstract: Pharmaceutically relevant methylene oxindoles are synthesized by a palladium(0)-catalyzed intramolecular chlorocarbamoylation reaction of alkynes. A relatively underexplored class of caged phosphine ligands is uniquely suited for this transformation, enabling high levels of reactivity and exquisite *trans* selectivity. This report entails the first transition-metal-catalyzed atom-economic addition of a carbamoyl chloride across an alkyne.

The palladium-catalyzed carbohalogenation of unsaturated C–C bonds has emerged as a robust method for the synthesis of organic halides.^[1] Although significant advances in the area of alkene carbohalogenation have been demonstrated,^[2] reports using alkynes remain scarce.^[3] To this end, we recently described a stereodivergent Pd-catalyzed alkyne carbohalogenation reaction using aryl halides, which relied on the combined steric bulk of both catalyst and substrate to promote the desired reactivity (Scheme 1a).^[3c] Depending on the nature of the terminal alkyne substituent and the temperature of the reaction, both the *cis* and *trans* vinyl halide products could be accessed by a Pd-mediated isomerization process. During this investigation, we noticed that aryl halides **1'** bearing an amide tether were not suitable substrates for this transformation, giving only trace amounts of methylene oxindole **2** under various conditions (Scheme 1b). Our motivation for accessing this structural manifold lies in its frequent occurrence in a number of bioactive molecules and pharmaceuticals^[4] as well as its synthetic utility in target-oriented synthesis.^[5] Considering the limited number of methods available to access 3-(halomethylene)oxindoles in a highly stereoselective fashion, we sought to access this motif through an alternative disconnection employing carbamoyl chlorides **1** as precursors.^[6]

An analysis of the literature revealed that in contrast to acid chlorides and chloroformates,^[7] carbamoyl chlorides have not been frequently exploited in transition-metal-catalyzed alkyne addition reactions, despite their potential for accessing valuable N-containing heterocycles.^[8] Moreover,



Scheme 1. a) Stereodivergent vinyl halide synthesis by Pd-catalyzed alkyne carbohalogenation. b) Alternative synthetic routes towards the 3-(halomethylene)oxindole scaffold. c) Palladium-catalyzed formal carbiodination of alkenes using aliphatic carbamoyl chlorides.

the proposed chlorocarbamoylation reaction is a completely unknown process.^[9] A recent report by Tong and co-workers illustrated the synthetic potential of alkene-tethered carbamoyl chlorides in a Pd-catalyzed formal carbiodination reaction (Scheme 1c).^[2f] It should be noted that in the absence of NaI, the organochloride product could not be obtained, suggesting that Pd/dppe is not a suitable catalyst for promoting the elusive C_{sp^3} –Cl reductive-elimination step.

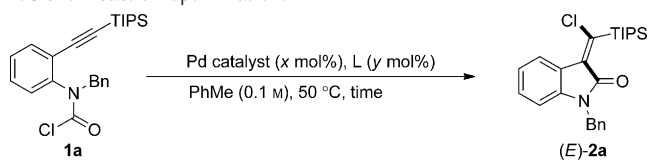
Herein, we report that aryl phosphaadamantane (PA-Ar) ligands (PA-Ar = 1,3,5,7-tetramethyl-2,4,8-trioxa-6-aryl-6-phosphaadamantane) are uniquely suited to promote the Pd⁰-catalyzed intramolecular chlorocarbamoylation of alkynes, representing the first application of these caged phosphine ligands in a C–Cl bond-forming reaction.^[10] Furthermore, the transformation proceeds with exquisite *trans* selectivity, which seemingly disobeys the requirement for a *cis* carbopalladation in the alkyne insertion step. Although the *cis*→*trans* isomerization of vinyl palladium species has been well-documented in intermolecular cross-couplings,^[11] there are few systems that enable the exclusive formation of the *trans* isomer in intramolecular alkyne addition reactions.^[12]

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Taking into account the importance of steric bulk in promoting carbon–halogen reductive elimination, carbamoyl chloride **1a** was chosen for the reaction optimization (Table 1). Initial screening revealed that both Pd(PtBu₃)₂ and Pd(Q-Phos)₂ were inefficient catalysts for the chlorocarbamoylation reaction, giving low yields of **2a** (entries 1 and 2). Upon switching to Pd(PtBu₂Ph)₂, a significant increase in reactivity was observed (entry 3). Attempts to push the

Table 1: Reaction optimization.



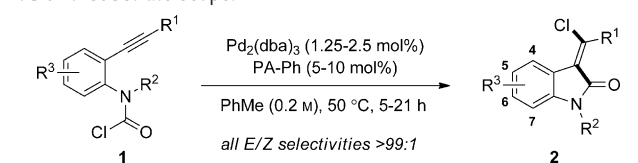
Entry	Pd catalyst (x mol %)	Ligand (y mol %)	Time [h]	Conv. ^[a] [%]	Yield ^[a] [%]	E/Z ^[a] [%]
1	Pd(PtBu ₃) ₂ (5)	–	18	19	12	N.D. ^[b]
2	Pd(Q-Phos) ₂ (5)	–	18	28	21	N.D. ^[b]
3	Pd(PtBu ₂ Ph) ₂ (5)	–	18	92	86	> 99:1
4	Pd ₂ dba ₃ (2.5)	PA-Ph (10)	3	100	99	> 99:1
5 ^[c]	Pd ₂ dba ₃ (1.25)	PA-Ph (5)	5	100	99	> 99:1
6 ^[c]	Pd ₂ dba ₃ (1.25)	PA-Ph (5)	21	26	8	> 99:1
7 ^[c]	–	PA-Ph (5)	5	7	0	–
8 ^[d]	Pd(OAc) ₂ (10)	dppf (30)	24	24	< 2	N.D.

[a] Conversions, NMR yields, and E/Z ratios were determined by ¹H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. NMR yields of the major isomer are given. [b] Formation of other side products prevented clear determination of the E/Z ratios by ¹H NMR analysis of the crude reaction mixture. [c] Concentration: 0.2 M. [d] With NaI (4.0 equiv), 0.067 M, reflux. N.D. = not determined.

reaction to full conversion by switching to higher temperatures and/or catalyst loadings were met with failure. It should be noted that in all cases, the *E* isomer, formally resulting from a *trans* addition process, was observed as the major product. In search of a more efficient catalyst, we were prompted to investigate ligands based on the phosphadamantane core, as its steric bulk and electronic properties are comparable to those of a PtBu₂ group and a P(OR)₂ group, respectively.^[13] Furthermore, these ligands are stable to air, moisture, and column chromatography, making them particularly attractive for reaction development. After screening a variety of PA-Ar ligands (Supporting Information, Scheme S1), PA-Ph proved to be the best, providing **2a** in 99% yield (E/Z > 99:1) after 3 h (entry 4).^[14] At higher concentration and longer reaction times, the catalyst loading could be decreased to 1.25 mol% (entry 5). Entries 6 and 7 demonstrate that maintaining a 1:2 Pd/L ratio is crucial for the reactivity, and that the reaction does not proceed in the absence of Pd. Notably, applying Tong's conditions^[2f] to substrate **1a** led to inferior results (entry 8).

With our optimized conditions in hand, we then investigated the substrate scope (Table 2). Substrates with electron-withdrawing substituents at the 5- (**1b**, **1c**, **1e**) or 6- position (**1h**, **1j**, **1k**) were well tolerated. Substrate **1f** demonstrated excellent reactivity, but more electron-rich

Table 2: Substrate scope.

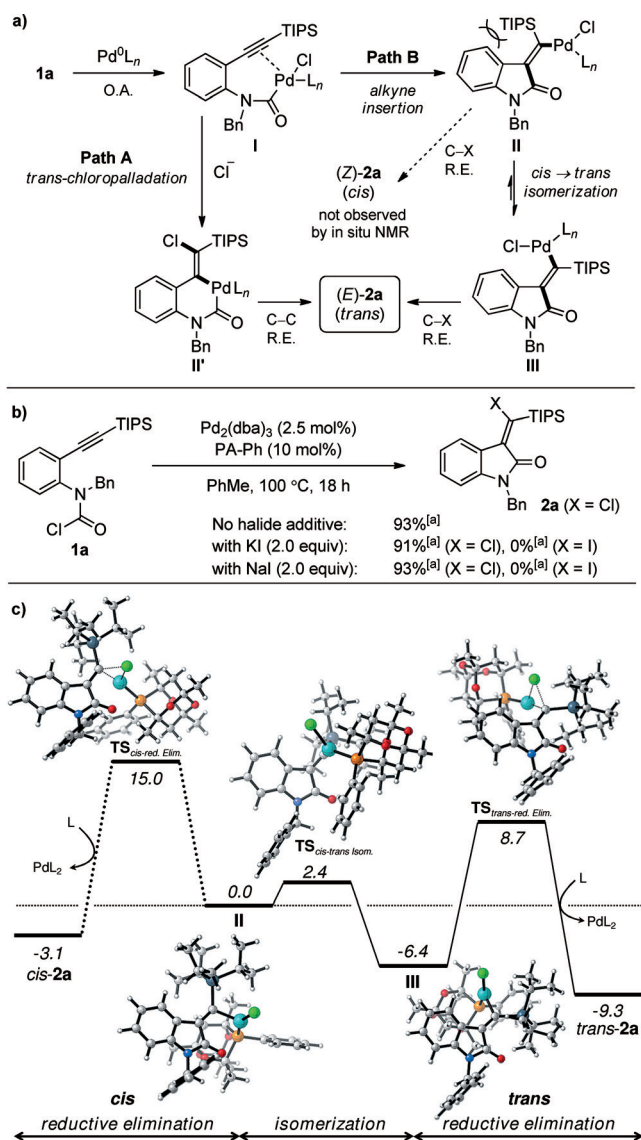


Substrate	Yield [%]	E/Z [%]
R = H (2a)	96%	
R = CN (2b)	77%	
R = F (2c)	98% ^[a]	
R = Cl (2d)	88%	
R = NO ₂ (2e)	85% ^[a]	
R = Me (2f)	99%	
R = OMe (2g)	85% ^[b]	
R = F (2h)	94% ^[b]	
R = Cl (2i)	97% ^[b]	
R = CF ₃ (2j)	93%	
R = OCF ₃ (2k)	98% ^[a]	
R = PMB (2l)	99%	
R = Me (2m)	96%	
R = CH ₂ Cy (2n)	95%	
R =  (2o)	93%	
R = TBS (2s)	71%	
R = TES (2t)	4% ^[c]	
R = Ph (2u)	0%	
R = Mes (2v)	0%	

[a] Pd₂(dba)₃ (2.5 mol %), PA-Ph (10 mol %). [b] Pd₂(dba)₃ (2.5 mol %), PA-Ph (10 mol %), 100 °C. [c] Yield determined by ¹H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard.

carbamoyl chlorides (**1g** and **1r**) were significantly less reactive under the standard conditions. Having additional Cl atoms on either the aromatic backbone (**1d**, **1i**) or the benzyl group (**1p**) did not compromise the reaction. However, the presence of a more reactive C_{sp}²–Br bond (**1q**) did have a negative impact on the yield. The reaction efficiency was minimally impacted upon changing the nature of the N-protecting group (**1l**–**1o**), but having a bulky silyl alkynyl substituent proved to be necessary (**1s** vs. **1t**). Aryl substituents were incompatible with the standard reactions conditions (**1u** and **1v**). In all examples, exclusive selectivity for the *E* isomer (> 99:1) was observed. To confirm our stereochemical assignment, an X-ray crystal structure of (*E*)-**2b** was obtained, and the E/Z ratios for all other examples were determined by comparing analogous chemical shifts in the ¹H NMR spectra.^[15]

To account for the high *trans* selectivity, we propose two possible mechanistic pathways (A or B) and present experimental and computational data that support pathway B (Scheme 2a).^[16] Both catalytic cycles begin with oxidative addition of Pd⁰ into the carbamoyl chloride bond. In pathway A, an in situ released chloride ion (from another molecule of **1a**) could trap intermediate **I** by a *trans* chloropalladation process, which, upon C–C reductive elimination, would give (*E*)-**2a**. To test the feasibility of an ionic pathway, we conducted the reaction in the presence of exogenous halide additives (KI or NaI, Scheme 2b).^[17] In both cases, **1a** was fully converted into **2a** (X = Cl) with no halide exchange products observed in the ¹H NMR spectrum of the crude reaction mixture, thus disfavoring pathway A. Alternatively,



Scheme 2. a) Proposed mechanism. b) Halide exchange experiments. [a] NMR yield determined by ¹H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. c) Gibbs free energy pathway calculated at the CPCM (toluene) M06L/def2-TZVP//B3LYP/6-31G(d) (LANL2DZ) level of theory (in kcal mol⁻¹).

in pathway B, *cis* carbopalladation would generate vinyl Pd species **II**. C–Cl reductive elimination would initially lead to (*Z*)-**2a**, which could re-enter the catalytic cycle and undergo a Pd-mediated isomerization process. When the reaction was monitored by in situ NMR spectroscopy, we did not observe the formation of (*Z*)-**2a** at the time intervals examined.^[14] In fact, we observed the exclusive and immediate formation of (*E*)-**2a** at a rate comparable to the rate of starting-material disappearance. This suggests that direct C–Cl reductive elimination from **II** is highly disfavored, and that a fast *cis*→*trans* isomerization (**II**→**III**) occurs.

To gain further insight, we undertook computational studies of path B in Scheme 2, employing the method M06L/def2-TZVP along with the solvation model CPCM (for toluene).^[18,19] Following oxidative addition, alkyne insertion

in intermediate **I** was calculated to proceed with a barrier of $\Delta G^\ddagger = 14.7$ kcal mol⁻¹. The subsequent *cis*→*trans* isomerization of **II** to the more stable intermediate **III** was found to be facile ($\Delta G^\ddagger = 2.4$ kcal mol⁻¹) and hence significantly favored over direct reductive elimination from **II** (Scheme 2c). Overall, isomerization followed by reductive elimination from **III** is the kinetically and thermodynamically favored pathway. The TIPS group was found to be crucial in easing the *cis*→*trans* isomerization as well as lowering the energetic span,^[20] thereby improving catalytic efficiency. The latter was also found to be the likely origin of the superior activity of the PA-Ph ligand.

In conclusion, we have developed a highly efficient palladium-catalyzed intramolecular chlorocarbonylation reaction that provides access to methylene oxindole scaffolds. The steric bulk and electron-deficient nature of the PA-Ar ligands make them ideal for promoting difficult reductive eliminations. The developed method demonstrates exquisite selectivity for the *E* isomer, thus representing a rare instance of a highly selective formal *trans* carbopalladation pathway.^[12]

Experimental Section

A 2 dram vial was charged with Pd₂dba₃ (2.9 mg, 0.00313 mmol, 1.25 mol %), PA-Ph (3.7 mg, 0.0125 mmol, 5 mol %), and **1a** (106.5 mg, 0.25 mmol, 1.0 equiv). After purging the reaction mixture with a flow of argon for 15 min, anhydrous toluene (1.25 mL) was added. The vial was sealed with a Teflon-lined cap and placed in a preheated oil bath at 50 °C. After 5 h, the reaction mixture was cooled to room temperature and passed through a plug of silica gel, washing with Et₂O. The solvent was removed under reduced pressure, and the crude mixture was purified by column chromatography.

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Keywords: chlorocarbonylation · cyclization · homogenous catalysis · palladium · phosphaadamantane

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